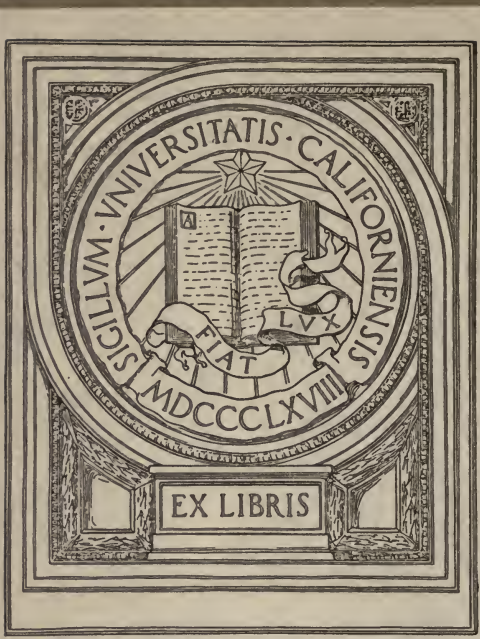
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THERMODYNAMICS AND CHEMISTRY

BY

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PREFACE

No one can write on thermodynamics without being deeply influenced by Willard Gibbs and Max Planck. The writings of the former will always be the admiration (and sometimes the despair) of the student of thermodynamics on account of the extreme rigor and completeness with which he discusses the subject, while Planck in his Lectures on Thermodynamics has given a treatment which is a model of conciseness, accuracy and logic. It has been my endeavor to write a book which, in addition to being accurate, logical and sufficiently rigorous, will furnish the student with numerous examples of the application of the principles of the science. It is with this object in view that four chapters have been devoted to the phase rule and its applications.

According to the point of view adopted in the following pages, thermodynamics is an empirical science, i.e., it is based on generalizations from experience which find their expression in the First and Second Laws. Hypothetical views as to the constitution of matter or the nature of heat are not used in the development of thermodynamic principles and hence these principles are as certain as the experimental facts on which they are based. It is of course possible to develop the subject on the basis of the kinetic theory, assuming heat to be the kinetic energy of molecules. This method has many advantages and may lead to a more intimate knowledge of nature than is gained when we refrain from such hypothetical aids. On the other hand, by developing thermodynamics empirically, we can be sure that all our results will be expressed in terms of quantities such as temperature, pressure, volume, etc., which can be determined directly by experiment. It is true that we shall frequently apply our empirical thermodynamic principles to problems which are set forth in the language of the molecular theory, as in the case of the study of ionic equilibrium. The distinction

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between hypothesis and fact is, however, always emphasized, so that the reader should never have any difficulty in determining to what extent a given result is hypothetical.

This book has been written to meet the needs of advanced students of Chemistry. While a course in thermodynamics is indispensable to students of physical chemistry, it is no less desirable for the organic chemist, who finds that, to an ever increasing degree, he must make use of physico-chemical methods and laws, the full significance of which will hardly be clear to one who is not familiar with their thermodynamic foundations. Moreover, the instructor in general or analytical chemistry, if he is not already acquainted with the principles of thermodynamics, will find that a knowledge of them will be of great service to him both in the class-room and in the laboratory. Many of the laws which we meet with in text-books of Chemistry are valid only under certain definite conditions. Chemical literature is full of instances in which writers have employed these laws in cases in which they are no longer valid. An exact knowledge of the conditions under which these laws may be applied would have prevented this waste of time and energy.

In addition to possessing a fair knowledge of chemistry and physics, the student of thermodynamics should be familiar with the elements of the differential and integral calculus. It is more important that he should understand the language than that he should be familiar with the results of the calculus. No apology is offered for the considerable number of mathematical equations which will be found throughout the book. They are as essential as chemical equations in a book on descriptive chemistry.

Errors of various kinds have doubtless escaped the eyes of the proof-readers. The author will be grateful to anyone who will be so kind as to call his attention to any error which may be found in the following pages.

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UNIVERSITY OF MINNESOTA,
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Thermodynamics and Chemistry

CHAPTER I

TEMPERATURE

In our every-day experience we describe bodies as hot or cold, basing our statements usually on the sensations we have when we bring our hands in contact with the objects considered. If we have before us a number of bodies, we may even attempt to arrange them in a series such that each member is hotter than the succeeding one. This property of bodies, which gives rise to the sensations of which we have been speaking, is called their temperature. Now, although our sensations inform us as to qualitative differences of temperature, they are not sufficiently accurate to be used as a quantitative measure of those differences, especially since experience shows that in some cases they may give erroneous results. Some more objective measure of temperature must be found. Now, it is an empirical fact that, other conditions remaining the same, most bodies have a greater volume when they are hot than when they are cold; and this fact can be established under such conditions that our sensations are certain to give us the correct qualitative result. We shall therefore measure changes in temperature by the changes in volume which certain bodies undergo, when all other conditions which might cause a change in volume (such as increased pressure) are maintained constant. Before proceeding, however, to a consideration of the various thermometric substances i.e. substances whose changes in volume are used to measure differences of temperature, it may be well to state two fundamental empirical

laws in regard to temperature. The first is that if two bodies A and B have each of them the same temperature as a third body C, then the temperature of A is the same as that of B; the second empirical law is that if a number of bodies, A, B, C, etc., have the same temperature and if a body M has a temperature higher than that of A, then its temperature is higher than that of B, C, etc.

If any number of bodies, originally at different temperatures, are placed in contact with one another, we know by experience that ultimately all will have the same temperature. The system is then said to be in temperature-equilibrium. If we confine our attention to two bodies originally at different temperatures, we know by experience that the temperature of the hotter body will fall, that of the colder body will rise. We describe this fact by saying that the hotter body loses heat and the colder body gains heat. It is the difference in the temperatures of the two bodies which determines the direction of the transfer of heat. Methods of measuring the quantity of heat transferred will be discussed later.

Thermometry

If we wish to use a particular body A as a thermometer, we note its volume when it is in temperature-equilibrium with melting ice (under a pressure of one atmosphere) and then when it is in temperature-equilibrium with water boiling under a pressure of one atmosphere. The change in volume represents a definite difference in temperature which we might take as unity, but which it is customary to take as equal to 100 units of temperature-difference, each unit being called a degree. This gives us the centigrade scale. The temperature of melting ice is then 0° C. and that of boiling water, 100° C. If the volumes of our substance A at 0° C. and 100° C. be V_0 and V_{100}, respectively, then, when the substance A has the volume V, the temperature will be $\frac{V - V_0}{V_{100} - V_0} \times 100 = t°$ C. Evidently a second substance B might be used in the same way to define the centigrade scale and since its volume changes do not necessarily follow the same law as those of substance A, the scale, as defined by B, would probably

differ at all points (except at 0° C. and 100° C.) from our first scale. Hence there arises a certain arbitrariness in the choice of a thermometric substance, since there is no reason *a priori* why one substance should be preferred to another. A definition of temperature which is independent of any particular substance can only be reached on the basis of the second law of thermodynamics. For the present, then, we must simply recognize the arbitrariness of our temperature scale, although we shall see that the one obtained using such gases as hydrogen, helium or nitrogen does not differ appreciably from the thermodynamic scale.

Among the various substances which have been used for measuring temperatures, we may mention mercury, alcohol, pentane, hydrogen, nitrogen, helium and air. Since the gases mentioned give temperature scales which are almost identical, there is evidently some justification in using a gas thermometer as a standard. For the most accurate work, however, the differences in the behavior of these gases must be taken into account and the particular gas used as a thermometric substance has to be borne in mind. A comparison of the various thermometric scales can be found in Landolt-Börnstein's Tabellen. Other methods of measuring temperature, such as those based (1) on the electrical resistance of metals, (2) on the electromotive force at the junction of two different substances and (3) on the radiation emitted by hot bodies, need only be referred to in this place.

Equation of State or Condition

Confining our attention to a homogeneous, isotropic body of uniform temperature and density, we can state as an empirical fact that the state of the body is determined by its mass m, its volume V, its temperature t, its state of electrification and magnetization, its surface and its chemical composition. For our present purpose we can omit the consideration of electrical, magnetic and surface effects. Accordingly all properties of a given body will be determined by its mass, volume and temperature. This is, for instance, true of the pressure acting on the body and exerted by the body on its surroundings. The pressure p is expressed in terms of the force acting on unit area of the surface

of the body; i.e., it is measured in dynes per cm.^{2}. The unit of pressure so defined $\left(1 \text{ bar} = \frac{1 \text{ dyne}}{\text{cm.}^2}\right)$ is, however, not the one commonly used. Pressures are usually expressed in millimeters of mercury or in atmospheres, an atmosphere being represented by a column of mercury at 0° C., 76 cm. high, at sea-level and 45 degrees latitude. Taking the density of mercury at 0° C. as 13.596, an atmosphere is equal to the weight of $76 \times 13.596 = 1033.3$ grams on a square centimeter, and since the weight of a gram at sea-level and 45 degrees latitude is 980.6 dynes, 1 atmosphere is equal to $76 \times 13.596 \times 980.6 = 1{,}013{,}250$ dynes per cm.^{2}. One megabar, or 10^6 dynes per cm.^{2}, is approximately one atmosphere; more accurately it is represented by a column of mercury 75.006 cm. high.

Now the pressure exerted by a body of mass m, volume V and temperature t, depends on the temperature and the ratio of mass to volume; for if we maintain the temperature constant, we can double the mass and simultaneously the volume without changing the pressure. Hence, if the specific volume be represented by $v = \frac{M}{V}$, we can say that for any homogeneous, isotropic body the pressure is a function of the specific volume and of the temperature or $p = f(v, t)$. This equation, whether it can be written explicitly or not, is called the equation of state of the body and is characteristic of the body.

Ideal Gases

The relation between the pressure, volume and temperature of most gases can be represented with a considerable degree of accuracy by a very simple equation. Gases for which this equation holds strictly are called ideal or perfect. The general form of the equation will be deduced from the laws of Boyle and of Charles and from our arbitrary definition of the temperature scale, using the gas thermometer. In a later section, the manner in which actual gases deviate in their behavior from that of ideal gases will be studied.

Now, according to our definition of temperature, using a gas

as a thermometric substance (and this is equivalent to the law of Charles), a gas under constant pressure increases uniformly in volume with the temperature. Let us suppose we have 1 gram of a gas at 0° C. under a pressure p_0 and a volume v_0. The volume v_t under the same pressure p_0 will be $v_t = v_0 (1 + \alpha t)$, where, according to our definition of temperature and Charles's law, α has the same value for all gases. Multiplying each side of this equation by p_0 we have $p_0 v_t = p_0 v_0 (1 + \alpha t)$. Now, according to Boyle's law, the product of the pressure and volume of a given mass of gas is a constant if the temperature is constant. In the above equation, v_t is the volume of 1 gram of the gas at $t°$ C. and under a pressure p_0. Let v represent the volume at $t°$ C. under a pressure p; then, according to Boyle's law, $pv = p_0 v_t$. But $p_0 v_t = p_0 v_0 (1 + \alpha t)$. Hence,

$$pv = p_0 v_0 (1 + \alpha t). \tag{1}$$

Introducing the numerical value of α, which is $\frac{1}{273}$ (more accurately $\frac{1}{273.09}$), equation (1) becomes $pv = \frac{p_0 v_0}{273} (273 + t)$. If we now define a new temperature scale such that its zero is 273 degrees below zero centigrade and such that each degree is equal to a degree centigrade, and if we represent this temperature by T and call it the absolute temperature, our last equation becomes

$$pv = \left(\frac{p_0 v_0}{273}\right) T. \tag{2}$$

Equation (2) may be written in the form

$$pv = rT, \tag{3}$$

where $r = \frac{p_0 v_0}{273}$ is the specific gas constant and is characteristic for each gas. If we desire to write the equation of state for m grams of an ideal gas, where V, the volume, equals mv, equation (3) evidently becomes

$$pV = mrT. \tag{4}$$

The value of r for any gas (assumed to be ideal) can be obtained from the equation $r = \frac{p_0 v_0}{273}$ where v_0 is the specific volume of the

gas at 0° C. and a pressure p_0. If the gas is at a pressure of 1 atmosphere, r is equal to the specific volume divided by 273. Table I contains the density of a number of gases at 0° C. and a pressure of 1 atmosphere and the values of the specific gas constant r in atmosphere —cc. per degree.

TABLE I

Gas	Density in $\frac{\text{gm.}}{\text{cm.}^3}$	r in $\frac{\text{atm. cc.}}{\text{degree}}$
Hydrogen	0.00008987	40.745
Oxygen	0.0014290	2.562
Nitrogen	0.0012507	2.928
Air	0.0012928	2.832
Carbon monoxide	0.0012504	2.929

If, instead of dealing with 1 gram of the different gases, we take as our standard quantity 1 cubic centimeter at 0° C., and 1 atmosphere we shall still have an equation of the form $pv = kT$. But since, when $T = 273$, $p = 1$ and $v = 1$, the value of k is $\frac{1}{273}$ and is the same for all gases in so far as they may be considered as ideal gases. It is clear that if we take any other definite volume at 0° C. and 1 atmosphere as a standard, we shall obtain a constant in the gas law equation which will be the same for all gases. The question then arises as to whether or not there is any particular volume which naturally suggests itself as a unit. From the purely physical point of view, the gram and the cubic centimeter are natural and logical units. But since our chief interest is in chemistry, we must ask ourselves if there is any chemical unit which can find a natural expression in the gas laws. To answer this question we must make a brief survey of some of the fundamental laws and theories of chemistry.

Molecular and Atomic Weights

Whenever hydrogen and oxygen are combined to form water, the proportion by weight as found by numerous experimenters is always constant, within the limit of experimental error. The

value obtained may be represented by the proportion: 1 gram of hydrogen to 7.94 grams of oxygen. This is a particular case of a general fact, which finds its expression in Dalton's Law of Definite Proportions by Weight. This may be briefly characterized by the statement that every compound substance has a fixed composition by weight. Thus the compositions of hydrochloric acid and of hydrogen sulphide are, respectively, 1 gram of hydrogen to 35.2 grams of chlorine and 1 gram of hydrogen to 15.9 grams of sulphur. Another important fact is that we may have compounds of the same elements in different proportions. Thus the composition of sulphur dioxide is 15.9 grams of sulphur to 15.88 grams of oxygen, while that of sulphur trioxide is 15.9 grams of sulphur to 23.82 grams of oxygen. Notice that 15.88 is 2×7.94 and 23.82 is 3×7.94. The generalization from numerous facts such as these is the Law of Combining Weights, viz.: it is possible to select a definite weight for each element which we may call the combining weight of the element, and to express the composition of all compound substances in terms of these combining weights or simple multiples of them. It will be clear to the reader that different chemists might arbitrarily select different combining weights for the same element, for the composition of any compound containing oxygen could be expressed just as easily using 15.88 as the chemical unit of oxygen, as by employing the number 7.94. We are, therefore, still in need of some general and definite rule by means of which we shall be able to select some one number for each substance which shall stand as the chemical unit weight of that substance.

The atomic theory of Dalton is an attempt to account for the laws of chemical combination enunciated above. He supposes that all substances consist of very small particles called atoms; the atoms of any one substance having the same weight, and that chemical combination is due to union between a definite small number of atoms of one kind with a small number of atoms of another kind. This theory evidently is consistent with the law of definite proportions by weight and the law of combining weights. The relative weights of these atoms, taking that of the atom of hydrogen as unity, are called the atomic weights. We have still

however no means of deciding between 7.94 and 15.88 as possible atomic weights of oxygen.

The next step in the historical development of our subject leads us to Gay-Lussac's Law of Combining Volumes, more accurately called the Law of Integral Proportions by Volume. This generalization states that in all reactions in which gases take part, the relative volumes of the different gases can be expressed by integers, usually small. Thus 2 volumes of hydrogen unite with 1 volume of oxygen to form 2 volumes of water vapor, each gas measured at the same pressure and temperature. Or again, 1 volume of hydrogen unites with 1 volume of chlorine to form 2 volumes of hydrochloric acid gas. The following conclusion is therefore justified: equal volumes of different gases at the same temperature and pressure contain either the same number of atoms or numbers of them in the different cases which stand to one another in proportions expressible by small integers. A very natural assumption and one put forward by Ampère is that the numbers are the same. Evidently this assumption, if adopted, would give us a definite unambiguous rule for determining atomic weights of gaseous substances, both elementary and compound. The reader must bear in mind that the name "atom" was originally applied to the smallest parts of a compound substance as well as to those of a simple substance. We shall employ this assumption, and shall find that it ends in contradiction. Applying it to one case only, that of the union of hydrogen and chlorine, since 1 volume of hydrogen + 1 volume of chlorine give 2 volumes of hydrogen chloride, 1 atom of hydrogen + 1 atom of chlorine must give 2 atoms of hydrogen chloride. Accordingly 1 atom of hydrogen chloride must contain $\frac{1}{2}$ atom of hydrogen and $\frac{1}{2}$ atom of chlorine; and the atoms of hydrogen and of chlorine must each consist of two parts, to each of which, and not to the whole, the name atom would more properly be applied.

The way out of the difficulty was pointed out by Avogadro who maintained that one must distinguish between two kinds of ultimate particles which, in modern notation, are called molecules and atoms, a molecule being a system which may contain

any number of atoms, like or unlike. Avogadro's assumption or hypothesis is that equal volumes of different gases under like conditions contain the same number of molecules. This hypothesis leads without difficulty to a determination of the relative molecular weights of gases and incidentally to a determination of atomic weights. Let us apply Avogadro's hypothesis to the same reaction to which we applied Ampère's assumption. We obtain the following result: 1 molecule of hydrogen + 1 molecule of chlorine give 2 molecules of hydrogen chloride. Hence 1 molecule of the compound must contain half a molecule of hydrogen and half a molecule of chlorine. The molecules of hydrogen and chlorine therefore consist of at least two atoms. The assumption that they contain two atoms only is justified by the kinetic theory of gases. On this basis, if the atomic weight of hydrogen be taken as 1, its molecular weight must be taken as 2. The molecular weight of any other gas will evidently be "n" times 2, if the gas is "n" times as heavy as hydrogen. From the known densities of the gases, we should obtain the following molecular weights: oxygen 31.76; chlorine 70.4, etc. In practice, however, oxygen is taken as a standard, for the reason that oxygen unites with more elements than does hydrogen and hence combining weights are frequently determined directly in terms of oxygen and only indirectly in terms of hydrogen. For that reason we shall take 32.00 as the molecular weight of oxygen, and therefore 2.016 as that of hydrogen. Since 32 grams of oxygen occupy 22.4 liters at 0° C. and 1 atmosphere, the molecular weight of any gas may be defined as the weight of 22.4 liters at 0° C. and 1 atmosphere. We are next led to define the atomic weight of any element as the smallest weight of that element which occurs in the molecular weight of any of its gaseous compounds. Table II contains the results obtained in the case of a number of substances.

Avogadro's hypothesis has been confirmed by so many independent methods that it has lost a great deal of its hypothetical character and will be made use of in this book without hesitation. Like the laws of Boyle and of Charles, Avogadro's rule is strictly true of ideal gases only. But since actual gases, as we shall see,

TABLE II

Substance	Molecular weight	Atomic weight
Hydrogen	2.016	1.008
Oxygen	32.000	16.000
Ammonia	17.03	.....
Water	18.02	.....
Chlorine	70.92	35.46
Hydrogen chloride	36.47	.....
Nitrogen	28.02	14.01
Phosphorus (vapor)	124.0	31.0
Mercury (vapor)	200.6	200.6

can be made to approach very closely the state of perfect gases, the true molecular weight of an actual gas can be obtained with great accuracy.

We have then obtained an answer to our question as to what quantity of a gas is to be taken as our chemical unit and the answer is: the molecular weight in grams or approximately 22.4 liters at 0° C. and 1 atmosphere. If M represents the molecular weight in grams of an ideal gas, then equation (4) becomes, for this mass of gas, $pV = MrT$. We shall use the abbreviation "mole" for the molecular weight in grams. The value of Mr is evidently $\frac{pV}{T}$, and if we take $T = 273$ and $p = 1$ atmosphere, V has the same value for all ideal gases, hence Mr is a constant, having the same value for all ideal gases. Representing Mr by R, we arrive at the following equation for 1 mole of an ideal gas,

$$pV = RT \tag{5}$$

or for n moles,

$$pV = nRT. \tag{6}$$

When the temperature is 273.09 degrees absolute and the pressure is 1 atmosphere, the gram-molecular volume is 22.412 liters (see next chapter). Hence the numerical value of $R = \frac{pV}{RT}$ is

$$\frac{1 \times 22.412}{273.09} = .08207 \frac{\text{liter-atm.}}{\text{degree}}.$$

Evidently $R = 82.07 \frac{\text{atm.} \cdot \text{cc.}}{\text{degree}}$, or, in absolute units, since 1 atmosphere is $1{,}013{,}250 \frac{\text{dynes}}{\text{cm.}^2}$,

$$R = 83.16 \times 10^6 \frac{\text{ergs}}{\text{degree}}.$$

Let us now consider how the behavior of an ideal gas can be deduced from equation (5). We shall keep one of the three variables p, V, and T constant and study the relation between the other two.

Behavior at Constant Pressure. (Isobaric changes.) The coefficient of expansion α is defined as the ratio of the increase of the volume to the volume at 0° C., when the gas has its temperature raised 1 degree centigrade at constant pressure p. Thus, since $pV_T = RT$, $pV_{T+1} = R(T + 1)$ and $pV_0 = R \times 273$, we have

$$\alpha = \frac{V_{T+1} - V_T}{V_0} = \frac{1}{273}.$$

Using the notation of the calculus,

$$\alpha = \frac{1}{V_0}\left(\frac{dV}{dT}\right)_p = \frac{p}{R \times 273} \cdot \frac{R}{p} = \frac{1}{273}.$$

Behavior at Constant Volume. (Isochoric changes.) The coefficient of increase of pressure β is defined as the ratio of the increase of the pressure to the pressure at 0° C. when the temperature of the gas is raised 1 degree at constant volume. We have then $p_0V = R \times 273$, $p_TV = RT$ and $p_{T+1}V = R(T + 1)$. Accordingly $\beta = \frac{p_{T+1} - p_T}{p_0} = \frac{1}{273}$ and is equal to α, the coefficient of expansion. In the language of the calculus,

$$\beta = \frac{1}{p_0} \cdot \left(\frac{dp}{dT}\right)_V = \frac{V}{R \times 273} \times \frac{R}{V} = \frac{1}{273}.$$

Behavior at Constant Temperature. (Isothermal changes.) The coefficient of compressibility is defined as the ratio of the infinitesimal diminution of unit volume to the infinitesimal

increase of pressure, the temperature being kept constant. It is therefore equal to $\left(-\frac{dV}{V}\right)_T = \frac{1}{p}$. The reciprocal of the compressibility coefficient is the coefficient of elasticity, which, for isothermal changes, is therefore equal to p.

The three coefficients considered are not independent. For every substance there is an equation of state $p = f(v, T)$. Hence $dp = \left(\frac{dp}{dv}\right)_T dv + \left(\frac{dp}{dT}\right)_v dT$. Applying this equation to changes at constant pressure we easily get

$$\left(\frac{dv}{dT}\right)_p = \frac{\left(\frac{dp}{dT}\right)_v}{-\left(\frac{dp}{dv}\right)_T} \quad \text{or} \quad \left(\frac{dp}{dT}\right)_v = \frac{\frac{1}{v_0}\left(\frac{dv}{dT}\right)_p}{-\frac{1}{v_0}\left(\frac{dv}{dp}\right)_T} = \frac{\alpha}{K},$$

where α and K are the coefficients of expansion and compressibility respectively and $\left(\frac{dp}{dT}\right)_v$ is p_0 times the coefficient of increase of pressure $\beta = \frac{1}{p_0}\left(\frac{dp}{dT}\right)_v$.

Mixture of Ideal Gases

If two gases at the same original pressure and temperature are brought in contact with each other, it will be found that after a certain time the two gases have formed a physically uniform mixture under a pressure equal to the original one and a volume equal to the sum of the original volumes. This at least is approximately true of actual gases and is assumed to be strictly true for ideal gases. The total pressure exerted by the mixture on the walls of the containing vessel is supposed to be due to the sum of the partial pressures exerted by each gas. (Dalton's Law of Partial Pressures.) Let us suppose that we have a mixture of $n_1, n_2, n_3, \ldots$ moles of gas 1, gas 2, gas 3, etc., respectively, in a total volume V and at a temperature T. Assuming that each gas exerts a pressure independently of the others and letting

p_1, p_2, p_3, . . . be the partial pressures of the different gases, we have the following relations:

$$p_1V = n_1RT,$$
$$p_2V = n_2RT,$$
$$p_3V = n_3RT.$$

Adding these equations, and representing the total pressure by p, we obtain

$$pV = (p_1 + p_2 + p_3 \ldots)\, V = (n_1 + n_2 + n_3 \ldots)\, RT$$

or
$$pV = \sum n_1RT. \tag{7}$$

Defining the concentration c of a substance as the number of moles per liter, we evidently have for each gas in the mixture an equation of the form

$$p_1 = \frac{n_1RT}{V} = c_1RT. \tag{8}$$

When the pressure is measured in atmospheres, the volume in liters and the concentration in moles per liter, R has, as shown previously, the numerical value 0.08207. Evidently we have also the relation

$$p = (p_1 + p_2 + p_3 + \ldots) = (c_1 + c_2 + c_3 + \ldots)\, RT. \tag{9}$$

The composition of a gas mixture may also be expressed in terms of mole fractions. Thus the mole fraction x_1 of gas 1 is

$$\frac{n_1}{n_1 + n_2 + n_3 +} = x_1.$$

Now since $pV_1 = n_1RT$ and $pV = (n_1 + n_2 + n_3 + \ldots)\, RT$, we have also the relation

$$x_1 = \frac{p_1}{p}, \tag{10}$$

which defines the mole fraction of a given gas in terms of its partial pressure and the total pressure.

If we define the term partial volume of a gas in a mixture as the volume which the gas would occupy if under the total pressure of the mixture, and if we represent the partial volumes by V_1, V_2, V_3, . . . , then we evidently have $pV_1 = n_1RT$, pV_2

$= n_2RT$, etc. Hence $p(V_1 + V_2 + V_3 + \ldots) = (n_1 + n_2 + n_3 + \ldots)RT = pV$. Therefore $V_1 + V_2 + V_3 \ldots = V$ (the total volume), and

$$\frac{V_1}{V} = \frac{n_1}{n_1 + n_2 + n_3 + \ldots} = x_1. \qquad (11)$$

PROBLEMS

1. When the temperature is defined by a gas thermometer, the linear expansion of copper is given by the formula $l_t = l_0(1 + at + bt^2)$ where $a = 1.670 \times 10^{-5}$ and $b = 4.03 \times 10^{-9}$. If we, however, define temperatures by means of a copper thermometer in which equal increases in length of a copper rod correspond to equal intervals of temperature and if we define 0° and 100° C. in the usual way, what temperature will the copper thermometer indicate when the gas thermometer indicates 50° C.?

2. Deduce the law of multiple proportions from the law of definite proportions and the law of combining weights.

3. The mass of 1 liter at 0° C. and 1 atmosphere and the composition of some gaseous carbon compounds are as follows: ethylene, 1.250 grams, 85.71 per cent carbon and 14.29 per cent hydrogen; propane, 1.964 grams, 81.82 per cent carbon and 18.18 per cent hydrogen; carbon dioxide, 1.964 grams, 27.27 per cent carbon and 72.73 per cent oxygen. From these data, determine the atomic weight of carbon.

4. Calculate the mole fractions, the concentrations and the partial pressures of the components of a mixture consisting of 10 grams of hydrogen, 16 grams of oxygen and 42 grams of nitrogen, the temperature being 0° C. and the total volume 11.2 liters.

5. In the case of air at the constant pressure of 1 atmosphere, 1 cc. at 0° C. becomes 1.3671 cc. at 100° C.; if, however, the volume is kept constant, the pressure increases from 1 atmosphere at 0° C. to 1.3665 atmosphere at 100° C. What are the absolute zeros (in degrees centigrade) on the constant pressure and the constant volume air thermometers?

CHAPTER II

ACTUAL GASES

In this chapter we intend to study the behavior of real gases and in order to indicate how it differs from that of ideal gases we shall frequently employ geometrical methods. Let us therefore picture to ourselves the behavior of ideal gases by using the geometrical equivalents of some of the algebraic equations of the last chapter. We shall deal in all cases with one mole of the gas.

Isobars. If the pressure p is kept constant, we may write the following equation: $V = \frac{R}{p} \cdot T = k_1 T$. If the ordinates represent volumes and the abscissæ represent absolute temperatures, we get the series of curves given in Fig. 1 by taking different values of p. The curves are straight lines running through the origin and making an angle with the T-axis whose tangent is $\frac{R}{p}$.

Isochores. Keeping the volume constant, we have $p = \frac{R}{V} \cdot T = k_2 T$, represented in Fig. 2 by a series of straight lines going through the origin and making an angle with the T-axis whose tangent is $\frac{R}{V}$.

Isotherms. When the temperature is kept constant, we have $pV = RT = k_3$, represented in Fig. 3 by a series of rectangular hyperbolas.

We can also represent the isotherms as in Fig. 4, where the ordinates are equal to pV and the abscissæ stand for the pressures.

The pV-p diagram is well adapted to show any deviation from the ideal state, since the isotherms for ideal gases are straight lines parallel to the pressure axis. The departure of any real gas from the ideal state will be shown on a pV-p diagram by the extent to which the isothermal curves deviate from straight lines parallel to the axis of pressures. The general

behavior of gases may now be briefly stated. There is a certain temperature, characteristic of each gas, at which the value of pV remains essentially constant when the pressure is increased from

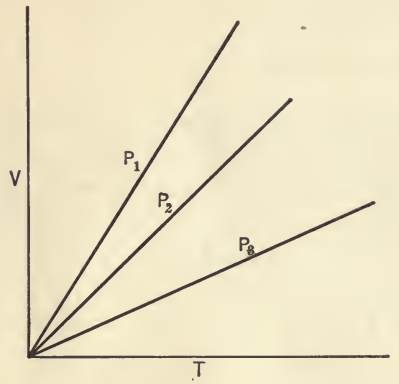


FIG. 1. Isobars

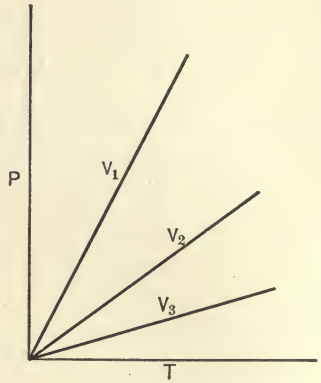


FIG. 2. Isochores

zero to moderately high values. At this temperature the gas obeys Boyle's law within a certain range of pressures with great accuracy. On the pV-p diagram, this would be represented

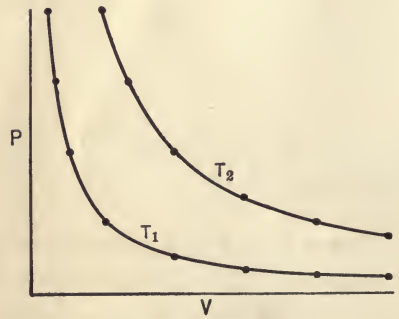


FIG. 3. Isothermals

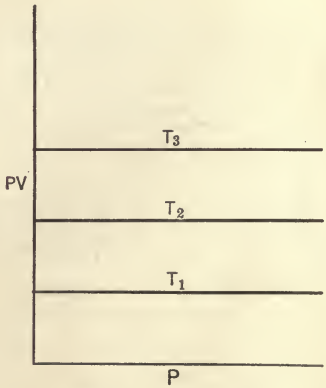


FIG. 4. Isothermals

by an isothermal parallel to the p axis over a considerable range of pressures. At higher pressures the isothermal bends upward; i.e., the value of pV increases at higher pressures. This characteristic temperature varies widely in the case of different gases;

for hydrogen,* it is $-165.72°$ C., for nitrogen it is about $52°$ C. and for CO_2 it would probably be above $400°$ C. For temperatures above this characteristic one, the value of pV increases with the pressure throughout the whole range from zero pressure to very high pressures. On the pV-p diagram, this behavior would be represented by an isothermal rising continuously with increasing pressure. This is true of hydrogen (and also of helium) at ordinary temperatures, but not of any other gases, whence Regnault called hydrogen the gas *plus que parfait*. Lastly in the case of temperatures below what we have called characteristic for the gas, the values of pV at first diminish, reach a minimum, then rise continuously with increase of pressure. This is the behavior commonly met with at ordinary temperatures in the case of most gases.

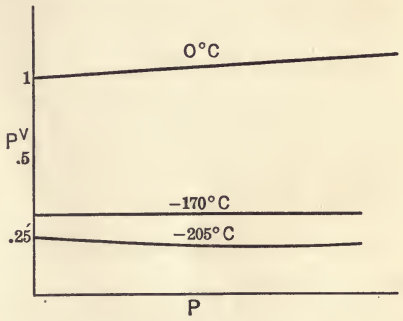


FIG. 5. Hydrogen

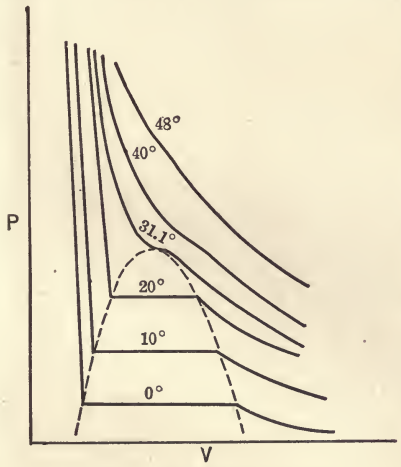


FIG. 6. Isothermals of CO_2

We have next to consider the phenomenon of liquefaction which occurs within a certain range of temperature whenever the pressure on a gas is increased to a sufficient extent. For many years, attempts to liquefy hydrogen, oxygen, nitrogen, carbon monoxide and a few others were unsuccessful, and these gases were frequently called permanent gases to distinguish them from those which could be condensed. The researches of Andrews† on

* Onnes and Braak, Comm. Phys. Lab. Leiden, No. 97 (1907).

† Phil. Trans., pt. ii, p. 575 (1869).

carbon dioxide and of many investigators since his time have shown that for every gas there is a critical temperature at and below which the gas can be liquefied, usually at a moderate pressure, whereas above this critical temperature, the gas cannot be condensed to the liquid state no matter how high a pressure is employed. The behavior of carbon dioxide, as found by Andrews, is typical of all gases and is represented on a p-V diagram in Fig. 6.

Equation of State for Actual Gases

Since actual gases deviate more or less from the behavior of ideal gases, it becomes a matter of practical importance to be able to express the pressure, volume and temperature relations of real gases as accurately as possible. The first noteworthy attempt in this direction was made by Van der Waals,* who, on the basis of considerations concerning the actual volume of the molecules and the forces of attraction between them, put forward the equation

$$p = \frac{RT}{V-b} - \frac{a}{V^2}, \tag{1}$$

in which b is a function of the actual volume of the molecules and a depends on the molecular forces of attraction.

Since it is our aim to avoid as far as possible the introduction of hypothetical views as to the nature of matter, we shall consider the equations of state of Van der Waals and of other investigators as more or less accurate, empirical statements of experimental facts. The equation of Van der Waals is supposed to be valid for the liquid as well as for the gaseous state. Now, although this equation depicts in a very striking way the behavior of gases, it does not do so quantitatively over considerable ranges of temperature and pressure, without a great deal of juggling with the constants a and b. Especially near the critical point is it highly inaccurate as it leads to results far removed from the facts. On this account many investigators have tried to formu-

* Continuität des gasförmigen und flüssigen Zustandes.

late expressions which would be more consistent with the facts, but the only one we shall mention here is that of Dieterici,* viz.:

$$p = \frac{RT}{V - b} e^{-\frac{a}{VRT}} \qquad (2)$$

in which a and b have approximately the same significance as in the equation of Van der Waals. In the Dieterici equation b is a function of the volume of the molecules and $\frac{a}{V}$ represents the work done by the molecules in passing through the surface layer. The applicability of the Dieterici equation and its superiority both theoretically and practically to that of Van der Waals have been shown in some detail by the author † in the case of a number of substances. In Fig. 7, the Dieterici equation $p = \frac{RT}{V - b} e^{-\frac{a}{VRT}}$ is plotted at three different temperatures for a substance using the following system of units. The mass of gas dealt with has a volume of 1 cm.^{3} at 0° C. and 1 atmosphere and the values of the constants are: $a = 0.008$ atm. cc.^{2} and $b = 0.002$ cc. The three temperatures selected are, on the absolute scale, 244.3, 271.5 and 298.6. The highest isothermal approximates to a rectangular hyperbola, the middle one has a horizontal inflexion at C, while the lowest one exhibits a maximum and a minimum point, B and E. The resemblance to the isothermals as found for an actual gas and as depicted in Fig. 6 is very striking. Evidently the isothermals correspond to temperatures above, at and below the critical temperature. For a temperature below the critical, the ordinary behavior of a gas on compression at constant temperature is not given by the curve *GFEDBAH* but by *GFDAH*. In other words, when the point F is reached, on further diminution of volume, some liquid in a state represented by the point A is formed and the process of condensation proceeds at constant pressure until the gas is completely condensed. We may therefore distinguish the two curves by the names, theoretical and actual isothermals. There is indeed evidence that part of the

* Ann. d. Physik. u. Chemie, **11**, p. 700 (1899).

† Journ. Amer. Chem. Soc., **38**, 528 (1916); **39**, 1229 (1917).

theoretical isothermal is realizable, for a gas can be compressed along the curve *FE* without condensation and a liquid can be expanded along the curve *AB*. The portion of the curve *BDE*,

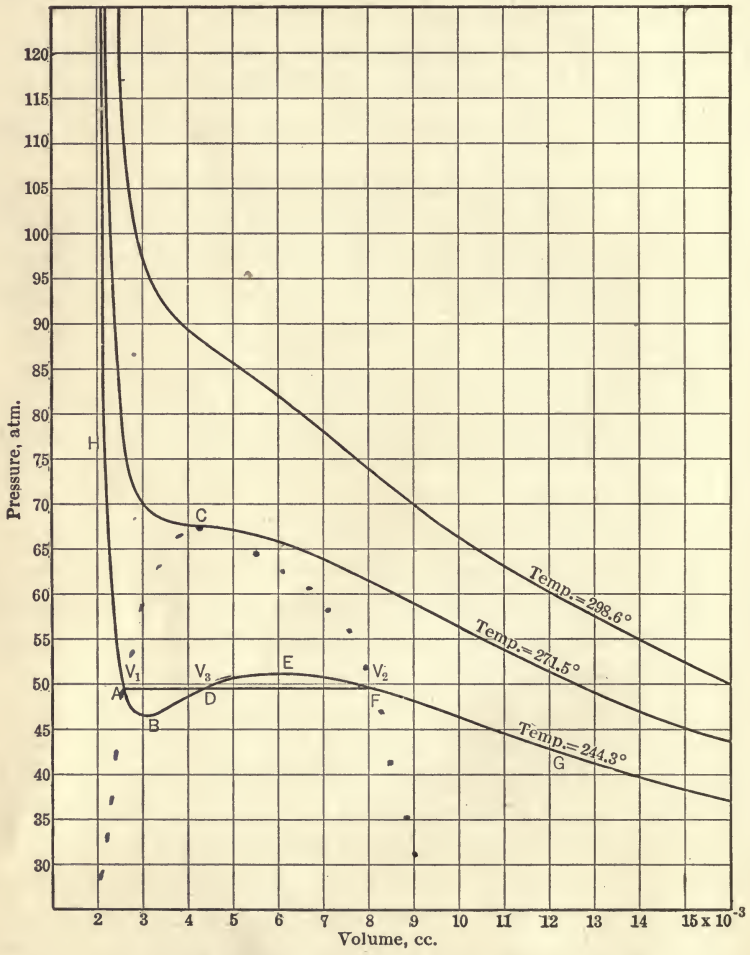


FIG. 7. Isothermals According to the Dieterici Equation

however, represents states that are probably unrealizable, since going from *B* to *E* would mean an increase in volume with increase in pressure and this can hardly correspond to anything that can be experimentally attained.

A very important point in connection with the Dieterici or the Van der Waals or any similar equation is that it leads to a prediction of a critical point and, moreover, permits the characteristic properties of the critical point to be calculated from the equation itself. Any horizontal line in Fig. 7 cuts the curve in three points, of which all may be real and unequal (represented by V_1, V_3, V_2), or all real and coincident (represented by the point C) or one real and two imaginary (for any horizontal line above the critical point). In other words, for given values of p and T there are in general three values of V and the critical point may be defined as the point at which these three values of V coincide. This definition can be used in the case of the Van der Waals equation in finding the coördinates of the critical point, since this equation may be written in the form of an equation of the third degree in V. For example, Van der Waals equation can be written

$$V^3 - \left(b + \frac{RT}{p}\right) V^2 + \frac{a}{p} \cdot V - \frac{ab}{p} = 0. \qquad (3)$$

A different method of defining the critical point and one that is of general application is deducible from the fact that at the critical point the critical isothermal has a horizontal inflexion, i.e., at this point the tangent to the curve is horizontal, and the curve also has an inflexion. These two properties are expressed mathematically as follows:

(1) condition for horizontal tangent, $\left(\frac{dp}{dV}\right)_T = 0.$

(2) condition for inflexion, $\left(\frac{d^2p}{dV^2}\right)_T = 0.$

Applying these conditions to both the Van der Waals and the Dieterici equations and representing critical quantities by the subscript c, we obtain the following set of relations:

Van der Waals	Dieterici
$V_c = 3b$	$V_c = 2b$
$T_c = \frac{8a}{27Rb}$	$T_c = \frac{a}{4Rb}$
$p_c = \frac{a}{27b^2}$	$p_c = \frac{a}{4e^2b^2} = \frac{a}{29.56b^2}.$

(4)

In place of the three constants a, b and R, the equations of state may be written using the three constants p_c, V_c, T_c. If we define the reduced temperature, pressure and volume of a substance by the equations, reduced temperature $\theta = \frac{T}{T_c}$, reduced pressure $\pi = \frac{p}{p_c}$, and reduced volume $\phi = \frac{V}{V_c}$, we obtain by substitution the following equations which no longer contain any constants characteristic of a particular substance:

$$\text{Van der Waals reduced equation, } \pi = \frac{8\theta}{3\phi - 1} - \frac{3}{\phi^2}.$$

$$\text{Dieterici reduced equation, } \pi = \frac{\theta}{2\phi - 1} e^{2 - \frac{2}{\theta\phi}}. \qquad (5)$$

It is easy to show that under moderate pressures and therefore large specific volumes, the two equations are essentially identical. At the critical point however there is a great divergence. Thus the value of the fraction $\frac{RT_c}{p_c V_c}$ is 2.67 (Van der Waals) and 3.695 (Dieterici). For a great many normal substances, Young* has found this ratio to be between the limits 3.67 and 3.93. For these substances at any rate the Dieterici equation should be much superior to the Van der Waals. The lowest value of the ratio obtained experimentally is 3.13 for helium,† and even this value is much higher than the one predicted by Van der Waals.

Gases at Low Pressures

Van der Waals' equation may be written in the form

$$pV = RT + p\left(b - \frac{a}{pV}\right) + \frac{ab}{V^2}.$$

At low pressures, this is evidently equivalent to

$$pV = RT + p\left(b - \frac{a}{RT}\right). \qquad (6)$$

Similarly the Dieterici equation $p(V - b) = RTe^{-\frac{a}{VRT}}$ becomes

$$pV - pb = RT\left(1 - \frac{a}{VRT}\right),$$

* Stoichiometry, p. 228 (1908).

† Quoted in Young's Stoichiometry, p. 212 (1918).

or $$pV = RT + p\left(b - \frac{a}{RT}\right),$$

identical with that of Van der Waals. As p approaches zero, $pV = RT$ and the gas approaches the ideal state, a conclusion confirmed by experiment. In the following discussion, we shall take as our unit volume of gas, the volume at 0° C. and 1 atmosphere. Hence, from equation (6),

$$1 = R \times 273 + b - a, \quad \text{or} \quad R = \frac{1 + a - b}{273}$$

and equation (6) may be written

$$pV = \frac{(1 + a - b)\,T}{273} + p\left(b - \frac{273\,a}{(1 + a - b)\,T}\right). \qquad (7)$$

Confining our attention to isothermals at 0° C., equation (7) will become

$$pV = (1 + a - b) + p\,(b - a). \qquad (8)$$

Since the gas becomes ideal when p is zero, we find that (pV) ideal $= 1 + a - b$, whereas (pV) actual $= 1$, when $p =$ 1 atmosphere and the actual volume $= 1$. If the gas were ideal, under the same pressure the volume would be $1 + a - b$. A knowledge of a and b is sufficient to enable us to determine what would be the density of an actual gas if it were to become ideal. Now the values of a and b can be calculated from the critical data, assuming the validity of the Van der Waals or the Dieterici or some other equation of state. Since, however, it has been found that a and b are functions of the temperature, a different plan must be followed. Rewriting equation (8) in the form

$$pV = 1 - A + pA = 1 + (p - 1)\,A \qquad (9)$$

and considering equation (9) as an empirical expression of the facts, the value of A is easily deducible from experiment, since

$$\left(\frac{d\,(pV)}{dp}\right)_{T=273} = A. \qquad (10)$$

In Table III are given a number of values of A.*

* Young's Stoichiometry, p. 45 (1918).

TABLE III

Gas	A	Observer
Oxygen	−0.00094	Rayleigh
Hydrogen	+0.00053	"
Nitrogen	−0.00056	"
Carbon monoxide	−0.00081	"
Carbon dioxide	−0.00668	"
Nitrous oxide	−0.00747	"
Nitric oxide	−0.00117	Jacquerod and Scheurer
Neon	+0.00105	Burt
Hydrogen chloride	−0.00748	Gray and Burt

For a given gas, when $p = 1$ atmosphere, $V = 1$ (equation (9)). When $p = 0$, i.e., when gas is in the ideal state, $pV = 1 - A$. If now the given gas were ideal when the pressure is 1 atmosphere its volume would be $1 - A$ instead of 1. If d represents the density of the actual gas when the pressure is 1 atmosphere and d_i the density if the gas were ideal under the same pressure, then evidently

$$\frac{d_i}{d} = \frac{1}{1 - A} \quad \text{or} \quad d_i = \frac{d}{1 - A}. \tag{11}$$

If M_1, M_2 are the molecular weights of two gases, it is easy to deduce the following equation

$$\frac{M_1}{M_2} = \frac{d_{i_1}}{d_{i_2}} = \frac{d_1}{d_2} \cdot \frac{1 - A_2}{1 - A_1}. \tag{12}$$

Let us calculate the exact molecular weight of hydrogen in terms of that of oxygen taken as 32, using equation (12), the values of A from Table III and the densities from Table I. We find

$$M_H = 32 \cdot \frac{0.00008987}{0.0014290} \cdot \frac{1.00094}{0.99947} = 2.0154$$

in excellent agreement with results obtained from chemical analysis. If D_0 represents the density of a gas with reference to oxygen at 0° C. and 1 atmosphere pressure, and if M is its exact molecular weight, then

$$M = 32\, D_0 \frac{1.00094}{1 - A}, \tag{13}$$

where A refers to the gas whose molecular weight is to be found. We can also calculate now the gram-molecular volume of an ideal

gas. The volume of 32 grams of oxygen at standard conditions is $\frac{32}{0.0014290} = 22{,}393$ cc. The volume if it were ideal is found to be $22{,}393 \times (1 - A) = 22{,}393 \times 1.00094 = 22{,}414$ cc. Berthelot takes 22,412 cc. as the best value and 273.09° as the temperature of melting ice on the absolute scale, whence our values for R were derived in Chapter I.

PROBLEMS

1. Find the value of $\left(\frac{dp}{dT}\right)_V$ for a mole of an actual gas, assuming the validity (1) of the Van der Waals equation, (2) of the Dieterici equation. How does it compare with the value for an ideal gas? Do the same for $\left(\frac{dp}{dV}\right)_T$, $\left(\frac{dV}{dT}\right)_p$ and $\left(\frac{d(pV)}{dp}\right)_T$.

2. Is there any temperature for which $\frac{p}{T}$ will equal $\frac{R}{V}$ in the case of a gas for which (1) the Van der Waals equation holds, (2) the Dieterici equation holds? If so, express it in terms of a, b and R.

3. Calculate the exact molecular weights of N_2, CO, CO_2, N_2O, NO and HCl from the following densities as well as from the data in Tables 1 and 3: CO_2, 0.0019768; N_2O, 0.0019777; NO, 0.0013402; HCl, 0.0016394. Compare the values obtained in this way with those determined by analysis.

4. Reversing somewhat the procedure in problem (3), and using molecular weights based on the accepted atomic weights, calculate the volume which one mole of each of the gases in problem (3) would occupy under standard conditions if it were an ideal gas.

CHAPTER III

HEAT

In our first chapter we stated that if two bodies at different temperatures are placed in contact, the temperature of one will fall, that of the second will rise until the temperatures of both are equal. Now there has been no change in the mass of either body, so that if anything has been transferred from the hotter to the cooler body, it is certainly not material in nature. But the volume of the hotter body has become smaller and that of the cooler body has become greater (at least, this is generally true) and we desire a name for the cause or agent which has produced these effects. We shall call it heat and say that the hotter body has lost heat and the colder body has gained heat. Evidently this is a purely experimental definition of the term. When we say that a body is gaining heat, we mean that it is in contact with a body at a higher temperature and that therefore its own temperature is rising. If we say a body is losing heat, we shall mean that the body is in contact with a body at a lower temperature. Since the flow of heat into a body raises its temperature we have a logical method of measuring the quantity of heat by taking as our unit that amount of heat which will raise the temperature of a definite amount of a standard substance through a definite number of degrees. Notice particularly that we have not defined heat as that which raises the temperature of a body, for the temperature of a body can be raised by compression or by an electric current, and although mechanical work and the electric current can produce the same effects as heat, they are not heat. We are interested here mainly in the transfer of heat and the measurement of the amount transferred, and according to our definition this transfer takes place only when bodies are in contact. The reader may be reminded of the common statement that heat is

transferred by conduction, convection and radiation. We shall not in this book consider radiant energy as heat, and as to transfer of heat by convection, that is evidently a special case of conduction by contact. We are not concerned here with molecular-kinetic theories which explain the loss of heat of a cooling body as due to the decrease in kinetic energy of the molecules of the body.

Unit Quantity of Heat. We shall call the unit quantity of heat a calorie and define it as the quantity of heat which will raise the temperature of 1 gram of water at atmospheric pressure one degree centigrade. Since this quantity has been found to depend on the initial temperature of the water, a further specification has to be made in regard to this point. Formerly the initial temperature was taken as 0° C., giving what is called the zero calorie; the 15° calorie has, however, been generally adopted in recent times, although the United States Bureau of Standards recommends the 20° calorie as more convenient. For most purposes it is sufficiently accurate to consider that a calorie will raise the temperature of 1 gram of water one degree centigrade as long as the initial temperature of the water is between 0° C. and 100° C. A larger unit of heat called the kilogram calorie (Cal.) is equal to 1000 gram calories (cal.).

Heat Capacity. The number of calories of heat necessary to raise the temperature of any system of bodies one degree centigrade is called the heat capacity of the system. In the case of a physically homogeneous system (such as a substance or a solution) we can speak of the heat capacity of one gram or the specific heat capacity, usually abbreviated to specific heat. The specific heat of a substance is, like other characteristic properties, a function of two independent variables, e.g., the pressure and the temperature, and these must therefore be fixed before the specific heat is determined. If we represent by Q the quantity of heat which raises the temperature of a gram of a substance from t_1 to t_2, then the mean specific heat of the substance C_m, from t_1 to t_2, is given by the equation

$$C_m = \frac{Q}{t_2 - t_1}. \qquad (1)$$

The strict definition of the (true) specific heat C of a substance will evidently be given by the equation,

$$C = \frac{q}{dt}, \tag{2}$$

where dt represents the infinitesimal elevation of temperature due to the infinitely small quantity of heat q. Since, however, experience shows that the specific heats of most substances change rather slowly with the temperature, the true specific heat at any temperature is in practice equal to the mean specific heat over a small temperature interval including the temperature in question.

Instead of dealing with the heat capacity of a gram of a substance it is often more convenient to consider the heat capacity of the gram-atomic or gram-molecular weight. The atomic heat is equal to the specific heat multiplied by the atomic weight; the molecular heat is obtained by multiplying the specific heat by the molecular weight.

Heat Capacity of Solids

The specific heat of solids is always determined under approximately constant pressure. In 1819 Dulong and Petit put forward the generalization that in the case of the solid elements, the atomic heat is approximately constant and equal to 6.4. The extent to which this law is valid may be seen by a study of Table IV. In the case of a number of the elements of low atomic weight, such as boron, carbon, and silicon, the atomic heat is lower than 6.4. Experiments at high temperatures show however that the atomic heats of these substances increase rather rapidly with the temperature, reaching a value of 5.5 at about 200° C. in the case of silicon, 985° C. in the case of diamond, and at a red heat in the case of boron. At extremely low temperatures, the specific heats of solids become very small, vanishing at the absolute zero. This may be illustrated by Table V, which gives the atomic heat of copper as determined by Nernst.*

* Ann. d. Physik., **36**, 295 (1911).

TABLE IV

Element	Specific heat	Atomic weight	Atomic heat
Lithium	0.941	7.0	6.6
Boron	0.238	11.0	2.6
Carbon (diamond)	0.117	12.0	1.25
Sodium	0.293	23.0	6.7
Magnesium	0.246	24.3	6.0
Aluminium	0.222	27.1	6.0
Silicon	0.170	28.3	4.8
Sulphur (rhombic)	0.173	32.0	5.5
Potassium	0.166	39.1	6.6
Calcium	0.170	40.0	6.8
Chromium	0.104	52.	5.4
Iron	0.110	56.	6.2
Nickel	0.108	58.7	6.4
Copper	0.0925	63.6	5.9
Zinc	0.0915	65.4	6.0
Bromine (solid)	0.0843	80.	6.7
Silver	0.055	108.	5.9
Cadmium	0.055	112.	6.2
Tin	0.05	119.	6.0
Iodine	0.0541	127.	6.9
Platinum	0.032	195.	6.2
Gold	0.031	197.	6.1
Mercury	0.032	200.6	6.4
Lead	0.0299	207.	6.2
Bismuth	0.030	208.	6.2
Uranium	0.028	238.2	6.5

TABLE V. ATOMIC HEAT OF COPPER

$t°$ C.	Atomic heat
−185.0	3.38
−186.0	3.33
−239.6	0.538
−245.3	0.324
−249.5	0.223

The law of Dulong and Petit is evidently an approximate statement of a fundamental law and many attempts have been made to find a more exact formulation. Further discussion of these points must be deferred to a later chapter.

Heat Capacity of Liquids

The specific heat of liquids usually (although not invariably) increases with the temperature, and the variation with the temperature is usually greater than in the case of solids. The specific heat of water decreases from 0° C. to a minimum at about 25° C. and then increases steadily. The following table gives information on this point with respect to a number of liquids.

Methyl alcohol	$c = 0.5634 + 0.002715\ t - 0.0000376\ t^2$
Ethyl alcohol	$c = 0.5396 + 0.001698\ t$
Propyl alcohol	$c = 0.5279 + 0.001692\ t$
Ether	$c = 0.5290 + 0.000592\ t$
Chloroform	$c = 0.2324 + 0.000101\ t$

No law for liquids, analogous to that of Dulong and Petit for solids, has been discovered.

Heat Capacity of Gases

On account of the relatively large volume changes which gases experience when the pressure or temperature is changed, it is absolutely necessary that the determination of the specific heat of gases should be carried out under conditions that can be specified accurately. There are three principal cases to be considered, (1) the specific heat at constant pressure (c_p); (2) the specific heat at constant volume (c_v); (3) the specific heat when the gas is maintained in equilibrium with the liquid form, called briefly the specific heat of saturated vapor (h). Table VI contains results for a number of gases.

TABLE VI. MEAN HEAT CAPACITIES (REGNAULT) BETWEEN 0° AND 100° AT CONSTANT PRESSURE

Gas	1 gram	1 liter, 0° C. and 1 atm.	1 mole
Air	0.2375	0.305	.....
Oxygen	0.2175	0.310	6.96
Hydrogen	3.4090	0.307	6.87
Nitrogen	0.2438	0.305	6.83
Carbon monoxide	0.2479	0.309	6.94
Chlorine	0.1214	0.38	8.6
Carbon dioxide	0.2025	0.398	8.91
Nitrous oxide	0.2238	0.440	9.85

The increase in the heat capacity of gases with the temperature is negligible in the case of monatomic gases, small in the case of diatomic gases, becoming greater the more complex the constitution of the gas. Table VII contains the molecular heat at constant volume for a number of gases, as given by Nernst.*

TABLE VII. VALUES OF C_v

Gas	0° C.	100°	300°	500°	1200°	2000°
Argon	2.98	2.98	2.98	2.98	2.98	2.98
H_2	4.75	4.78	5.02	5.20	5.8	6.5
N_2, O_2, CO, HCl	4.90	4.93	5.17	5.35	6.0	6.7
Cl_2	5.85	5.88	6.12	6.30	7.0	.....
H_2O	4.93	5.97	6.45	6.95	8.62	about 14
CO_2, SO_2	6.80	7.43	8.53	9.43	11.2	about 14
NH_3	6.62	6.82	7.41	8.52	....	.....
$(C_2H_5)_2O$	about 23	about 32.6	41.6	....	....	.....

PROBLEMS

1. 100 grams of lead at 100° C. are put in 200 grams of water at 20° C. and the resulting temperature is 21.22° C. Calculate the specific heat of lead.

2. If the mean molecular heat of nitrogen at constant pressure between 0° and $T°$ absolute is $6.50 + 0.0005\,T$, calculate the true molecular heat at 0° C.; at 100° C.

3. The value of C_p for water vapor up to 2000° C. is given by the equation $C_p = 8.81 - 1.9 \times 10^{-3}\,T + 2.22 \times 10^{-6}\,T^2$. Find the mean value of C_p for the intervals 0°–100° C.; 100°–200° C.; 100°–1000° C.

4. The specific heat of a certain solid element is 0.170 and its exact equivalent weight is 20.03. Assuming the law of Dulong and Petit, calculate the exact atomic weight of the element.

* Zeit. f. Elektrochemie, **17,** 272 (1911).

CHAPTER IV

THE FIRST LAW OF THERMODYNAMICS

Mechanical Work. In the science of mechanics work is measured by the product of a force and the distance through which the force acts in the direction of the force or $w = f.s.$ The unit of work (the erg) is done by unit force (the dyne) acting through unit distance (the centimeter). 1 erg = 1 dyne-cm. Since work is done in raising a weight against the force of gravity, work is frequently expressed in terms of what are called gravitational units. Thus the work done in raising a gram-weight vertically a distance of 1 cm. is called a gram-weight centimeter, or simply a gram-centimeter and since the weight of a gram is 980.6 dynes (at sea-level and 45° lat.), a gram-cm. is equal to 980.6 ergs. Evidently the value of this unit depends on the value of the acceleration of gravity at the place where the work is done. Mechanical work is also done whenever a body changes its volume while subjected to a pressure. We shall consider first the case in which the pressure remains constant while the volume changes. Suppose the body is in the form of a cylinder whose length is l cm. and whose cross-section is A cm.^{2}. Let p dynes per cm.^{2} be the pressure on the body. Then the force on the total cross-section is pA dynes. Let the increase in the volume of the body be ΔV and let us suppose that during the expansion the cross-section remains constant while the length of the cylinder increases by Δl cm. Then the work done is equal to the force $\times$ distance $= pA \cdot \Delta l$. But $A \cdot \Delta l = \Delta V$, therefore work done $= p \cdot \Delta V$ ergs. If the pressure does not remain constant during the expansion, we must consider an infinitely small increase of volume dV, under a pressure p, giving the infinitely small amount of mechanical work dW. Hence

$$dW = p\,dV, \tag{1}$$

or, for a finite change in volume,

$$W = \int_{V_1}^{V_2} p\, dV, \tag{2}$$

where V_1 and V_2 represent the initial and final volumes.

Equivalence of Heat and Work

In Chap. III when we were defining our use of the word heat it was stated that mechanical work and the electric current could bring about the same effects as a quantity of heat. Thus the temperature of a body can be raised by friction or by compression or by an electric current. Confining our attention to the effects produced by mechanical work, the question naturally arises whether or not a given amount of mechanical work is always equivalent to a fixed quantity of heat in raising the temperature of a system. The first quantitative experiments to determine this matter were carried out by Joule in 1843. In these experiments, weights falling through a certain distance caused stirrers to rotate in a mass of liquid, and the work done by friction brought about an elevation of temperature. At the conclusion of an experiment, all the materials were in the same state as at the beginning, except that the weights had fallen a certain distance, and the liquid, thermometer, stirrers, etc., were at a higher temperature. Now from mechanics the work done by the falling weights is equal to the work done by the force of friction. Knowing the heat capacity of the system whose temperature was changed, we can calculate the number of calories of heat which would have produced the same effect as the mechanical work of the falling weights. Since the time of Joule, many determinations of the mechanical equivalent of heat have been made, the result of which has been to show that a calorie of heat is equivalent to a fixed number of units of mechanical work. This number is called the mechanical equivalent of heat. We shall adopt the following value in this book:*

1 calorie (15° C.) = 42,690 gm.-cm. = 4.186×10^7 ergs.

* Landolt-Börnstein Tabellen (1912) p. 1266.

Electric Currents

A study of the properties of electricity has shown that electric currents are able to do mechanical work, e.g., drive a motor and lift weights. Experiment has shown that the passage of 1 coulomb of electricity under a pressure of 1 volt will do work equal to ten million (10^7) ergs. An electric current passing through a body raises the temperature of the body and here again there is a definite relation between the current and the heating effect, 1 volt-coulomb (1 coulomb under a pressure of 1 volt) being equivalent to $\frac{1}{4.186} = 0.2389$ calories.

Radiation. We could proceed to a discussion of the fact that the radiation emitted by a given body at a given temperature in unit time, when it is absorbed by any system, raises the temperature of the latter by a constant amount, and accordingly it would be possible to speak of a thermal equivalent of radiation. But we shall not dwell on this relationship here.

Chemical Processes. If a solution of an acid and a solution of a base, both at the same temperature, are mixed, we shall observe a rise in the temperature of the mixture. If the surroundings are maintained at the original temperature of the solutions, there will be a flow of heat from the mixture to the surroundings and a certain number of calories will be transferred before the mixture is at the original temperature. In this case also, which may be taken as typical of a chemical reaction, a certain process is equivalent, from our point of view at least, to a definite number of calories, and we may accordingly speak in a certain sense of the thermal equivalent of a chemical reaction.

Energy. We shall give the name energy to anything which can be converted directly or indirectly into heat and we shall express quantities of energy in the same units as quantities of heat, i.e., in calories or ergs. We shall speak of electrical energy, energy of radiation and chemical energy, and these together with heat and work may be called forms of energy. The total energy of a body would be found if we could cause it to reach a state in which it had lost all power to furnish heat or anything equivalent to heat. Now since this is impossible at present, or at any rate

impracticable, we must confine ourselves to measuring changes in the amount of energy possessed by a body or system of bodies when the body or system of bodies goes from one state to a second. We shall define the increase in energy of a body when it goes from a given initial state to a given final state as the algebraic sum of the thermal or mechanical equivalents of all effects produced in the system during the process. This means that all effects produced in the system are to be expressed in thermal or mechanical units (e.g., calories or ergs) and that the sum of these effects measures the increase in energy. From our definition of the increase in energy when a body goes from one state to another, it does not follow that this increase is independent of the way in which the process takes place. It is quite conceivable that the difference in energy in the two states might be determined by the nature of the process by which the body went from one to the other. The matter can be decided only by experiment and experiment has shown that the nature of the process does not affect the numerical value of the difference of energy in the two states. These experiments have led to a formulation of what we shall call the *First Law of Thermodynamics*, which may be stated as follows: The difference in energy of a system in two states depends only on the nature of the two states and is independent of the process by which the system goes from one state to the other. Let P_1 and P_2 (Fig. 8) represent in any suitable system of coordinates the two states of a system. Let U_1 be the energy of the system at the point P_1 and let U_2 be the energy of the system on arriving at the point P_2 along the curve P_1AP_2.

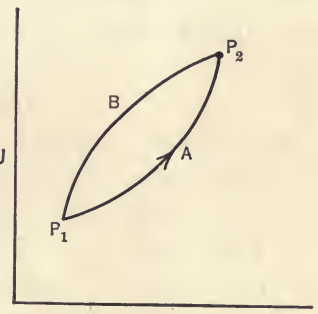


FIG. 8

According to the first law if we proceed from P_1 to P_2 along any other path, such as P_1BP_2, the system will have the same energy U_2 on reaching P_2. Evidently if we were to consider P_2 as the initial state and proceed to P_1 along either P_2AP_1 or P_2BP_1 the system would have the same energy at P_1 independent of

the path and since the difference in energy between the two states is constant, according to the first law, the system on reaching P_1 would have exactly its original amount of energy U_1. The energy of a system in a given state (even though we are unable to determine its absolute value) is therefore a quantity which is determined solely by the state itself and is therefore constant as long as the state does not change.

In order to express the First Law in a mathematical form, we shall make use of the following notation. Let Q stand for the quantity of heat absorbed by the system in any change, and let W represent the work furnished by the system to the surroundings (the term "work" including not only mechanical work, but electrical energy as well). Then for any change in which the system goes from state 1 to state 2, we have the following equality:

$$U_2 - U_1 = Q - W. \tag{3}$$

In the case of an infinitesimal change of state, equation (3) takes the form

$$dU = Q - W, \tag{4}$$

where Q and W represent infinitely small amounts of heat and work. They are not written dQ and dW because they are not in general differentials of a definite function.

Isolated System

If a system undergoes a change of state and is so bounded that all exchange of heat and work with the surroundings is made impossible, then from equation (3), since $Q = 0$ and $W = 0$, $U_2 - U_1 = 0$ or $U_2 = U_1$ and there is no change in the energy of the system. A system so constituted that all interchange of heat and work with the surroundings is excluded, is called an isolated system and one can therefore state that the energy of an isolated system is a constant quantity, irrespective of the processes, physical or chemical, which may occur in the system. From this point of view the First Law of Thermodynamics is often called the *Law of the Conservation of Energy*.

Cyclic Processes

If a system after undergoing any change returns to its original state, it is said to have completed a cycle. Applying equation (3) since $U_2 = U_1$, we have

$$0 = Q - W. \tag{5}$$

In other words, in any closed cycle, the work done by the system is equal to the heat absorbed. Equation (5) implies, therefore, that a perpetual motion machine, which must necessarily function in cycles and which would generate work out of nothing, is impossible.

It will, I hope, be clear to the student that the First Law of Thermodynamics or the Law of the Conservation of Energy is merely a generalized statement of the experience of mankind. It is a law which can be tested by further experimentation. Thus the failure of every attempt to construct a *perpetuum mobile* is added confirmation of the truth of the First Law. It can be tested by experiments planned to determine the change in energy when a system goes from one state to a second. If different values were to be found when the process was carried out in different ways, the First Law would fall to the ground. So far, however, experimental evidence is overwhelmingly in favor of the accuracy of the First Law, so overwhelmingly that its validity is no longer seriously questioned.

Units and Dimensions

Before proceeding to a study of the applications of the First Law, it may be useful to the student to have at his disposal a brief account of the subject of units and dimensions. Although this is a topic usually discussed in courses in physics and physical chemistry, it will be an advantage to the student of thermodynamics to have the subject matter fresh in his mind.

Fundamental and Derived Units. All the units in which physical quantities are expressed may be built up from a few units, called fundamental units. These may be selected in various ways, but for our purpose we shall adopt the units of length, mass, time and temperature as fundamental.

Unit of Length. The unit of length, the centimeter (cm.) is defined as the one-hundredth part of the standard meter preserved in Paris.

Unit of Mass. The unit of mass, the gram (gm.) is defined as the one-thousandth part of the mass of the standard kilogram preserved in Paris.

Unit of Time. The unit of time, the second (sec.), is defined as the one-eighty six thousand four hundredth part of a mean solar day.

Unit of Temperature. The unit of temperature, the degree, is defined as the one-hundredth part of the difference in temperature between melting ice and water boiling at a pressure of 1 atmosphere and is represented by a degree on the centigrade scale. (See Chap. I.)

From these fundamental units, others are derived in a systematic way. Thus the unit of area is 1 square centimeter ($cm.^2$), and the unit of volume is 1 cubic centimeter ($cm.^3$ or cc.). Another unit of volume is the liter, defined as the volume occupied by a kilogram of water at normal atmospheric pressure and at its temperature of maximum density. The liter is, within 2 or 3 parts in 100,000, equal to 1000 $cm.^3$. Here we shall consider 1 liter as identical with 1000 $cm.^3$.

Unit velocity is 1 centimeter per sec. or 1 $\frac{\text{cm.}}{\text{sec.}}$. Unit acceleration is 1 cm. per sec. per sec. or 1 $\frac{\text{cm.}}{\text{sec.}^2}$. Unit force = 1 dyne and is defined as the force which will impart unit acceleration to a mass of 1 gram. From the equation $f = ma$, where f is the force in dynes, m the mass in grams and a the acceleration in $\frac{\text{cm.}}{\text{sec.}^2}$, we see that 1 dyne = 1 $\frac{\text{gm. cm.}}{\text{sec.}^2}$. Unit work = 1 erg is done when 1 dyne acts through a distance of 1 cm. Accordingly, 1 erg = 1 dyne − cm. = 1 $\frac{\text{gm. cm.}^2}{\text{sec.}^2}$. A larger unit of work or energy is 1 joule = 10^7 ergs. The unit of pressure is 1 bar and is equal to 1 $\frac{\text{dyne}}{\text{cm.}^2}$. A larger unit is 1 atmosphere, defined as the pres-

sure of a column of mercury at 0° C. 76 cm. high at sea-level and 45 degrees latitude. Since 1 cc. of mercury at 0° C. has a mass of 13.596 grams and since 1 gram weighs 980.6 dynes,

$$1 \text{ atmosphere} = 76 \times 13.596 \times 980.6 = 1{,}013{,}250 \frac{\text{dynes}}{\text{cm.}^2}.$$

Units of Heat and Electricity

The unit quantity of heat, the calorie (cal.) has already been sufficiently defined. In regard to electricity, we shall give here only a few of the more useful units. The practical unit quantity of electricity is the coulomb defined as the quantity of electricity required to deposit 1.11800 milligrams of silver from a silver nitrate solution. An important unit of quantity of electricity is the *faraday* equal to 96,500 coulombs * and corresponding to the chemical equivalent weight of a substance. Currents are measured in amperes, 1 ampere being 1 coulomb per sec., while potential differences and electromotive forces are given in volts, the volt being defined, for practical purposes, by the statement that the E.M.F. of a standard cadmium cell at 20° C. is 1.0183 volts. The unit of electrical energy, 1 volt-coulomb, is equal to 1 joule or 10^7 ergs.

Dimensions

By the dimensions of any physical quantity, we mean an expression which shows the relation between the unit used in measuring the quantity and simpler units, especially the fundamental units of length, mass, time and temperature. Let us take as an example the quantity represented by pV where p is a pressure and V is a volume. We shall show that pV has the same dimensions as energy or work. Thus a pressure is a force per unit area and can be expressed in terms of $\frac{\text{dynes}}{\text{cm.}^2}$. Dynes can be expressed as $\frac{\text{gm. cm.}}{\text{sec.}^2}$, so that a pressure has the dimensions $\frac{\text{gm.}}{\text{cm. sec.}^2}$. Since a volume has the dimensions cm.^3, pV has the

* Bates & Vinal, Jour. Amer. Chem. Soc., **36**, 916 (1914)

dimensions $\frac{\text{gm.}}{\text{cm. sec.}^2} \times \text{cm.}^3$ or $\frac{\text{gm. cm.}^2}{\text{sec.}^2}$ and this expression is the same as that for an erg. In many cases we do not need to carry the analysis down to the fundamental units. Thus we may say that since a pressure can be expressed in terms of $\frac{\text{dynes}}{\text{cm.}^2}$ and a volume in terms of cm.^{3}, the quantity pV can be expressed in terms of $\frac{\text{dynes}}{\text{cm.}^2} \times \text{cm.}^3$ or dyne-cm. or ergs. If the pressure is given in atmospheres and the volume in liters, then the product of pressure and volume is so many liter-atmospheres and we know that a liter-atmosphere must be a unit of work or energy related to the erg. To find the exact relationship, all we have to do is to express atmospheres and volumes in terms of fundamental units. Thus 1 atmosphere = 1,013,250 $\frac{\text{dynes}}{\text{cm.}^2}$ and 1 liter = 1000 cm.^{3}. Hence, 1 liter-atmosphere = 1,013,250 × 1000 ergs = $\frac{1{,}013{,}250 \times 1000}{4.186 \times 10^7}$ = 24.205 cal.

In any expression which deals with physical quantities, all terms in the expression which can be added or subtracted must refer to quantities of the same physical nature and therefore of the same dimensions. As an illustration let us consider Van der Waals' equation in the form: $\left(p + \frac{a}{V^2}\right)(V - b) = RT$. We can make the following observations: the quantity b is of the same nature as V, i.e., is a volume, and if V is expressed in cm.^{3}, so must b be expressed in the same units. The expression $\frac{a}{V^2}$ must be of the same nature as p, and therefore a must have the dimensions of pV^2. If the pressure is measured in atmospheres and the volume in liters, a must be expressed in atmosphere-liters^2. Similarly RT must have the same dimensions as pV and, as we have previously shown, the dimensions are those of energy. The physical nature of R may be expressed by saying that it can be measured in terms of ergs per degree, or calories per degree or any other unit of work per degree. The heat capacity of a system is

obtained by dividing the number of calories added to the system by the elevation in temperature in degrees. Heat capacity is therefore expressed in terms of $\frac{\text{calories}}{\text{degree}}$ and accordingly we see that R has the same dimensions as heat capacity.

The results in Table VIII may be of use to the student.

TABLE VIII

	Ergs	Joules or Watt-sec.	15° cal.	Liter-atm.	Gram-cm.
1 erg =	1	10^{-7}	0.2389×10^{-7}	9.869×10^{-10}	1.0198×10^{-3}
1 watt-sec. = 1 joule =	10^{7}	1	0.2389	9.869×10^{-3}	1.0198×10^{4}
1 15° cal.	4.186×10^{7}	4.186	1	4.131×10^{-2}	4.2690×10^{4}
1 liter-atm.	1.0132×10^{9}	1.0132×10^{2}	24.205	1	1.0333×10^{6}
1 gram-cm.	9.806×10^{2}	9.806×10^{-5}	2.3425×10^{-5}	9.678×10^{-7}	1

In the equation $pV = RT$ for 1 mole of an ideal gas, the constant R has the following values in different units:

$$R = 8.316 \times 10^{7} \frac{\text{ergs}}{\text{degree}}$$

$$= 8.316 \frac{\text{joules}}{\text{degree}}$$

$$= 1.9865 \frac{\text{cal.}}{\text{degree}}$$

$$= 0.08207 \frac{\text{liter-atm.}}{\text{degree}}$$

$$= 84800 \frac{\text{gm. cm.}}{\text{degree}}.$$

PROBLEMS

1. Calculate the work done when the volume of a system changes by 120 cc. under a constant pressure of 15 atmospheres. Express the result in atmosphere-cc.'s, calories and ergs.

2. Express in liter-atmospheres the energy given to the surroundings when a kilogram of copper (specific heat, 0.0925) cools from 300° to 25° C.

3. A battery with an E.M.F. of 4 volts has its poles joined through a resistance. Battery and resistance form part of a calorimeter, the total heat capacity of which is 900. If the total resistance of the circuit is 1 ohm,

what will be the rise in temperature of the calorimeter after five minutes, if no heat is lost to the surroundings?

4. What are the dimensions of the quantity "a" of Van der Waals' equation?

5. Which of the two following equations is incorrect dimensionally, if "a" has the same meaning as in Van der Waals' equation?

$$\left(\frac{dp}{dT}\right)_v = \frac{p}{T}\left(1 + \frac{a}{VRT}\right) \quad \text{or} \quad \left(\frac{dp}{dT}\right)_v = \frac{p}{T}\left(1 + \frac{a}{VRT^2}\right).$$

6. In the equation, $\frac{\lambda}{T} = \left(V_2 - V_1\right)\frac{dp}{dT}$, λ represents a quantity of heat, V_2 and V_1 volumes, and p a pressure. What are the dimensions of each side of the equation?

CHAPTER V

APPLICATIONS OF THE FIRST LAW I

Homogeneous Systems

We shall now consider applications of the First Law to systems which are physically homogeneous. Although many of the results obtained will hold for heterogeneous bodies, it will perhaps be conducive to clearness if we start with a study of the simpler systems. The total energy U of any system, as pointed out in Chap. IV, is a single-valued function of the variables which determine the state of the system; it is therefore in general a function of the total mass m, the volume V, the pressure p, the temperature T and a number of variables which fix the composition of the system. Thus we may write

$$U = f(m, p, V, T, c_1, c_2, c_3, \ldots). \tag{1}$$

If we denote by v the specific volume of the homogeneous body, then $V = mv$ and we can rewrite equation (1) as follows:

$$U = f(m, p, v, T, c_1, c_2, c_3, \ldots). \tag{2}$$

In addition the body will have an equation of state, which may be written in the form:

$$p = \phi(v, T, c_1, c_2, c_3, \ldots). \tag{3}$$

Evidently by substituting the value of p from equation (3) in equation (2) we can express the latter thus:

$$U = \psi(m, v, T, c_1, c_2, c_3, \ldots). \tag{4}$$

We shall confine our attention to a homogeneous body in which the mass is invariable and the composition is either invariable or determined completely by the two variables v and T. Under these circumstances, the energy is a function of m, v and T, or m, V and T, and the pressure is a function of v and T only. In other words,

$$U = f_1(m, V, T) \tag{5}$$

and

$$p = f_2(v, T). \tag{6}$$

Evidently the value of U is determined not only by m, V, T, but by m, p, T, or m, p, V. We shall also suppose that in any changes that the system undergoes the work done by the system is given by the expression $W = \int_{V_1}^{V_2} p\,dV$ (see equation (2) Chap. IV); i.e., we shall suppose that the work consists entirely of the mechanical work due to volume changes of the system. With these provisos, bearing in mind the fact that m is constant, the First Law applied to our homogeneous body may be written

$$dU = Q - p\,dV, \tag{7}$$

or if we refer to 1 gram of the system, we shall employ the equation

$$du = q - p\,dv. \tag{8}$$

Specific Heats

The specific heat c of the homogeneous body is defined by the equation

$$c = \frac{q}{dT} = \frac{du}{dT} + p\frac{dv}{dT}. \tag{9}$$

Since however both u and v are functions not only of T but of p also, the values of $\frac{du}{dT}$ and $\frac{dv}{dT}$ are not determined unless more information about the process is given. In other words, the change in state is not determined simply by saying that the temperature has increased by dT. Accordingly, we shall have to define the specific heat by specifying an additional condition which the system has to satisfy. And we shall take as our first condition the requirement that the volume remains unchanged.

Constant Volume. Under these circumstances we obtain the relation for the specific heat at constant volume, c_v,

$$c_v = \left(\frac{du}{dT}\right)_v. \tag{10}$$

Constant Pressure. Let us suppose that the elevation of temperature dT takes place under constant pressure; then we obtain as the value of the specific heat at constant pressure, c_p,

$$c_p = \left(\frac{du}{dT}\right)_v + p\left(\frac{dv}{dT}\right)_v = \left(\frac{d(u + pv)}{dT}\right)_v. \tag{11}$$

The relation between c_p and c_v for any homogeneous body may be obtained in the following manner. Since u is a function of v and T, we may write

$$du = \left(\frac{du}{dT}\right)_v dT + \left(\frac{du}{dv}\right)_T dv, \tag{12}$$

or, at constant pressure,

$$\left(\frac{du}{dT}\right)_p = \left(\frac{du}{dT}\right)_v + \left(\frac{du}{dv}\right)_T \cdot \left(\frac{dv}{dT}\right)_p. \tag{13}$$

Substituting the value of $\left(\frac{du}{dT}\right)_p$ in equation (11) we obtain

$$c_p = \left(\frac{du}{dT}\right)_v + \left[p + \left(\frac{du}{dv}\right)_T\right] \left(\frac{dv}{dT}\right)_p \tag{14}$$

or finally

$$c_p = c_v + \left[p + \left(\frac{du}{dv}\right)_T\right] \left(\frac{dv}{dT}\right)_p. \tag{15}$$

Experiments of Gay-Lussac, Joule and Kelvin

Before applying the First Law to the case of gases, ideal or otherwise, we shall discuss briefly some experiments which throw light on the relation between the energy and the volume of a gas. The experiments of Gay-Lussac and the earlier ones of Joule consisted essentially in determining whether there is any change in temperature when a gas expands without doing work or without any heat exchange with the surroundings.

One vessel is filled with a gas and a second one is evacuated. By turning a stop-cock, the gas is allowed to flow from the first to the second until equilibrium is reached. Neither Gay-Lussac nor Joule was able to detect any change in temperature. Since in this experiment $q = 0$ and $w = 0$, $du = 0$ and from equation (12) $0 = \left(\frac{du}{dT}\right)_v dT + \left(\frac{du}{dv}\right)_T dv$. According to the experimental results, $dT = 0$, and $\left(\frac{du}{dT}\right)_v$ is, as we know, equal to c_v; therefore $\left(\frac{du}{dv}\right)_T$ is equal to zero. In words, the energy of a gas is a function of the temperature only. But we must add that there is

evidence that Gay-Lussac and Joule detected no change in temperature, not because there was no change, but because it was so small. It is highly probable that all actual gases would show a cooling effect in the experiment just described. In other words, in the equation $0 = \left(\frac{du}{dT}\right)_v \delta T + \left(\frac{du}{dv}\right)_T \delta v$, if applied to a small change in volume, δT is negative and hence for all actual gases $\left(\frac{du}{dv}\right)_T$ is positive. The matter was further studied by Joule and Kelvin who carried out experiments of a somewhat different kind. In these, a gas under a high pressure made its way slowly through a porous plug into a region where it was at a lower pressure, usually that of the atmosphere. After a certain time the state of the porous plug becomes stationary and as far as we are concerned can be disregarded. We shall consider the change in state of 1 gram of a gas before and after it has passed through the plug and we shall suppose that the quantities of the gas on each side of the plug are so large that the passage of 1 gram does not cause an appreciable change in pressure. Let the energy, pressure, volume and temperature of 1 gram of the gas be initially u_1, p_1, v_1, T_1 and finally u_2, p_2, v_2, T_2, where $p_1 > p_2$. We shall suppose the experiment so carried out that no heat flows into the gas from the surroundings or in the opposite direction. Since $q = 0$, the First Law gives us the relation

$$u_2 - u_1 = -w \quad \text{or} \quad u_1 - u_2 = w; \tag{16}$$

i.e., the loss in energy is equal to the work done by the gas on its surroundings. During the disappearance of 1 gram of the gas into the porous plug at constant pressure p_1, an amount of work equal to p_1v_1 is done on the gas. While the gram of gas is issuing from the plug at constant pressure p_2, it does an amount of work on the surroundings equal to p_2v_2. Accordingly the total amount of work w done on the surroundings by the gram of gas is $p_2v_2 - p_1v_1$. Hence, from equation (16),

$$u_1 - u_2 = p_2v_2 - p_1v_1 \quad \text{or} \quad u_1 + p_1v_1 = u_2 + p_2v_2. \tag{17}$$

A complete discussion of the Joule-Thomson or Joule-Kelvin effect cannot be given at this point, but we can nevertheless

draw a number of important inferences. Let us suppose that the gas used in the experiment is any gas other than hydrogen and helium and that the temperature is around 0° C. Let us also assume for the moment that during the experiment the temperature of the gas has not changed, i.e., that $T_2 = T_1$. Then we know that p_2v_2 is greater than p_1v_1 (see Chap. II), and hence u_2 is less than u_1. Now the experiments of Gay-Lussac and of Joule showed that $\left(\frac{du}{dv}\right)_T = 0$, (as a matter of fact, $\left(\frac{du}{dv}\right)_T$ is a small positive quantity), so that if the temperature is assumed to have remained constant, the energy of the gas will have remained constant or actually will have slightly increased. We must therefore conclude that the temperature does not in general remain constant. We may look at the matter in the following manner. First, in the case of all gases there will be a slight cooling due to the Gay-Lussac-Joule expansion; second, this cooling will be increased if p_2v_2 is greater than p_1v_1 and may be balanced or there may even be a rise in temperature if p_2v_2 is less than p_1v_1. A prediction as to what will occur necessitates a knowledge of the equation of state of the gas and some deductions from the Second Law of Thermodynamics. We shall therefore merely state that in the case of hydrogen (and presumably helium) a rise in temperature is observed, whereas with all other gases there is a fall in temperature in the Joule-Kelvin experiment. Since in these cases, as well as in the original experiments of Gay-Lussac and Joule, the temperature change is small, we shall extend our definition of an ideal gas by saying that its energy is a function of the temperature only; in other words, $\left(\frac{du}{dv}\right)_T$ or $\left(\frac{du}{dp}\right)_T$ is zero.

Returning now to equation (15), we can evidently write, for an ideal gas,

$$c_p = c_v + p\left(\frac{dv}{dT}\right)_p. \tag{18}$$

Or making use of the equation of state for 1 gram of an ideal gas, viz.: $pv = rT$, since $\left(\frac{dv}{dT}\right)_p = \frac{r}{p}$, we have on substitution in (18)

$$c_p = c_v + r. \tag{19}$$

If M is the molecular weight of the ideal gas, and if we denote the molecular heats by C_p and C_v, we easily obtain, since $R = Mr$ (see Chap. I),

$$C_p = C_v + R. \tag{20}$$

The difference between the molecular heats of an ideal gas at constant pressure and constant volume is a constant independent of the nature of the gas and equal to 1.987 calories per degree.

For an ideal gas equation (12) becomes

$$du = \left(\frac{du}{dT}\right)_v dT = c_v\, dT. \tag{21}$$

Evidently, if u is solely a function of T, the same may be said of c_v and hence of c_p (equation (19)). Measurements of the variation of c_p with the temperature have shown that over a considerable range c_p can be considered as practically constant. We shall accordingly extend our definition of an ideal gas once more by stating that its specific heat, either at constant pressure or at constant volume, is an absolute constant. With these definitions, we can integrate equation (21) and thus obtain

$$u = c_v T + \text{constant}, \tag{22}$$

where the value of the constant of integration depends on the standard state from which the energy is reckoned. Evidently we can write equation (22) in the form

$$u_2 - u_1 = c_v\,(T_2 - T_1), \tag{23}$$

which may perhaps be applied more easily to actual cases. Table IX gives the molecular heat, C_p, of a number of gases, the values of C_v as calculated by equation (20) and the value of $\gamma = \frac{C_p}{C_v}$, all at ordinary temperature.

TABLE IX

Gas	C_p	C_v	$\gamma = \frac{C_p}{C_v}$
Hydrogen	6.87	4.88	1.41
Oxygen	6.96	4.97	1.40
Nitrogen	6.83	4.84	1.41
Air (mole = 28.9 grams)	6.86	4.87	1.41
Carbon monoxide	6.94	4.95	1.40
Carbon dioxide	8.91	6.92	1.29
Nitrous oxide	9.85	7.86	1.25
Helium	4.97	2.98	1.67

Isothermal Process. Since the energy of an ideal gas depends on its temperature only, equation (7), applied to 1 mole of the gas, takes the form $0 = Q - p\,dV$,

or, for a finite change in volume,

$$Q = \int_{V_1}^{V_2} p\,dV. \tag{24}$$

Since, for a mole of the gas, $pV = RT$,

$$Q = \int_{V_1}^{V_2} \frac{RT\,dV}{V} = RT \log_e \frac{V_2}{V_1}. \tag{25}$$

If n moles of an ideal gas expand isothermally from an initial volume V_1 to a final volume V_2, the heat absorbed will be

$$Q = n\,RT \log_e \frac{V_2}{V_1}. \tag{26}$$

The integral, $\int_{V_1}^{V_2} p\,dV$, is also equal to the work done by the gas, so that, in this case, the heat absorbed is equal to the work done by the ideal gas. If p_1 and p_2 are the pressures corresponding to the volumes V_1 and V_2, since $p_1V_1 = p_2V_2$, we can evidently write the following for 1 mole of an ideal gas,

$$Q = W = RT \log_e \frac{V_2}{V_1} = RT \log_e \frac{p_1}{p_2}. \tag{27}$$

Adiabatic Process. We shall next consider the case in which an ideal gas undergoes a change, during which there is no exchange of heat with the surroundings, i.e., $Q = 0$. If we are dealing with 1 mole of a gas, equation (7) becomes

$$dU = -p\,dV. \tag{28}$$

But, for an ideal gas, $dU = C_v\,dT$ (equation (21)) and

$$p = \frac{RT}{V}, \quad \text{hence} \quad C_v\,dT = -\frac{RT\,dV}{V}$$

or $$C_v \frac{dT}{T} = -R\frac{dV}{V}.$$ If p_1, V_1, T_1 and p_2, V_2, T_2 represent the initial and final values respectively of the pressure, volume and temperature, we obtain, on integration,

$$C_v \log_e \frac{T_2}{T_1} = R \log_e \frac{V_1}{V_2}. \tag{29}$$

Therefore when a gas is expanded adiabatically, its temperature falls. Since $p_1V_1 = RT_1$ and $p_2V_2 = RT_2$, it is easy to obtain the following relations, where $\gamma = \frac{C_p}{C_v}$:

$$\gamma \log_e \frac{T_2}{T_1} = (\gamma - 1) \log_e \frac{p_2}{p_1} \tag{30}$$

$$p_1V_1^{\gamma} = p_2V_2^{\gamma}. \tag{31}$$

That is, if a gas is compressed adiabatically, the temperature rises; also by comparing equation (31) with one that holds for isothermal changes, e.g., $p_1V_1 = p_2V_2$, it is seen, since γ is greater than 1, that on adiabatic compression the volume diminishes more slowly than in the case of isothermal compression.

Work Done in Adiabatic Expansion. Equation (28), as we have seen, becomes, for an ideal gas,

$$-C_v\,dT = p\,dV, \tag{32}$$

the integral of which is

$$C_v\Big(T_1 - T_2\Big) = \int_{V_1}^{V_2} p\,dV = W, \tag{33}$$

which gives the mechanical work done when the volume of one mole of an ideal gas is changed adiabatically. In equation (33), V_1, T_1 and V_2, T_2 are the initial and final values respectively of the volume and temperature.

Reversible Processes. Equilibrium

A system is said to be in equilibrium when all the factors which determine the flow of energy or matter, either within the system itself or between the system and its surroundings, are exactly balanced. For example, the temperature throughout the system must be uniform and if the system is bounded by a wall permeable to heat, then the system and the immediate surroundings must have the same temperature. Moreover, if a system is enclosed in a vessel with a movable piston, the pressure exerted by the system on the piston must be exactly balanced by the pressure exerted by the piston on the system. If we have a gas, for example, in a vessel with a movable piston, and desire to change

the volume of the gas by a finite amount in a finite time, we must have a finite difference between the pressure exerted by the gas and the pressure exerted by the piston. If p and p' are the pressures of the gas and of the piston at any instant and if dV is the infinitesimal increase in volume of the gas, the work done by the gas is $p\,dV$, that done on the surroundings is $p'\,dV$ and the difference $(p - p')\,dV$ is equal to the kinetic energy of the system. In order that the work done on the surroundings shall be measured by $p\,dV$, there must evidently be no kinetic energy produced or the difference in the pressures p and p' must be infinitely small. In order to bring about a finite change, an infinite time would be required or the process must proceed infinitely slowly. At every stage in the process p and p' must differ only infinitesimally, i.e., at every stage in the process, the system and surroundings must be in equilibrium. A process carried out in this manner is called a reversible process. It is evidently characterized by the fact that an infinitesimal change in the value of the external pressure can reverse the direction of the change. By making the difference between p and p' small enough, we can approximate as closely as we desire to a reversible process.

Similar considerations will apply to a process in which heat is said to flow from one body to another at the same temperature, as when a gas is expanded isothermally and heat flows in from the surroundings to maintain the temperature constant. It is true that a transfer of a finite number of calories from one body to another can only take place in a finite time when there is a finite difference in temperature. If we make the difference of temperature infinitely small, the direction of flow will still be determined but the process will be infinitely slow. Here again an infinitesimal change in temperature is sufficient to reverse the direction of the flow of heat. Such a process as we have described will be a reversible isothermal exchange of heat and can, in practice, be approximated to as closely as is desired. It is evident from this discussion that reversible processes represent a limit to which actual processes may more or less closely approximate. Since, however, the properties of a system (such as the energy, density, pressure, etc.) in two states depend only on the two states and not

on the way in which the system has passed from one state to the other, the assumption of reversible processes is to be considered chiefly as a means of calculating the difference in the values of various functions of the system in the two states. Thus the difference in the entropy of a system in two states can be calculated by imagining the system to go from one state to another by a reversible process, but the difference in the entropy of the system in the two states is exactly the same, no matter by what process the change actually took place.

Carnot Cycle in Case of an Ideal Gas

We shall consider in this chapter one more application of the First Law to an ideal gas by supposing it to go through what is called a Carnot Cycle. This consists in a combination of two isothermal and two adiabatic processes at the end of which the system is in its original state. We shall imagine the process to be carried out with one mole of an ideal gas. We shall suppose that we have at our disposal two heat reservoirs, at temperatures T_2 and T_1 (where $T_2 > T_1$), which can be put in communication with the gas when necessary. The process can be represented graphically on a pressure-volume diagram as in Fig. 9.

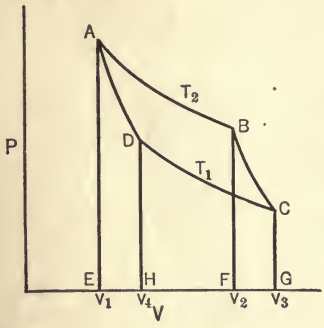


FIG. 9. Carnot Cycle

Starting at state represented by the point A in the figure, the gas is isothermally expanded to point B, then adiabatically to point C, then compressed isothermally to D, and finally adiabatically compressed to its original state A. Let the values of the pressure, volume and temperature of the mole of gas at the various points be as follows: at A, p_1, V_1, T_2; at B, p_2, V_2, T_2; at C, p_3, V_3, T_1 and at D, p_4, V_4, T_1. Let Q_2 be the quantity of heat absorbed by the gas from the heat reservoir during the isothermal expansion at T_2, and let Q_1 be the heat given out by the gas to the heat reservoir during the isothermal compression at T_1. Let W_1 and W_2 be the work done by the gas as it expands along AB and BC

and let W_3 and W_4 be the work done on the gas when it is compressed along CD and DA. If Q is the total heat absorbed by the gas in the whole process and if W is the total work done, then evidently

$$Q = Q_2 - Q_1,$$
$$W = W_1 + W_2 - W_3 - W_4. \tag{34}$$

Since the energy of the gas is the same at the end as at the beginning of the cycle,

$$Q = W. \tag{35}$$

Before calculating the values of Q_2, Q_1, W_1, W_2, W_3 and W_4, it will be advantageous to deduce a relationship between the volumes V_1, V_2, V_3 and V_4. Applying equation (29) to the adiabatic processes, we have for BC,

$$C_v \log_e \frac{T_2}{T_1} = R \log_e \frac{V_3}{V_2},$$

and for DA,

$$C_v \log_e \frac{T_2}{T_1} = R \log_e \frac{V_4}{V_1}.$$

Hence

$$\frac{V_3}{V_2} = \frac{V_4}{V_1} \quad \text{or} \quad \frac{V_2}{V_1} = \frac{V_3}{V_4}. \tag{36}$$

Stage 1. Isothermal Expansion, AB. For this stage the heat absorbed Q_2 and the work W_1 done by the gas are given by the following expressions (see equation (27)):

$$Q_2 = RT_2 \log_e \frac{V_2}{V_1}, \tag{37}$$

$$W_1 = RT_2 \log_e \frac{V_2}{V_1}. \tag{38}$$

Stage 2. Adiabatic Expansion, BC. In this process, the heat absorbed is zero and the work W_2 done by the gas (see equation (33)) is

$$W_2 = C_v (T_2 - T_1). \tag{39}$$

Stage 3. Isothermal Compression, CD. The heat evolved Q_1 and the work W_3 done on the gas are

$$Q_1 = RT_1 \log_e \frac{V_3}{V_4}, \tag{40}$$

$$W_3 = RT_1 \log_e \frac{V_3}{V_4}. \tag{41}$$

Stage 4. Adiabatic Compression, DA. The heat exchange is zero and the work W_4 done on the gas is

$$W_4 = C_v (T_2 - T_1). \tag{42}$$

Summing up, and bearing in mind equation (36), we have for the total heat Q absorbed by the gas,

$$Q = Q_2 - Q_1 = R (T_2 - T_1) \log_e \frac{V_2}{V_1}, \tag{43}$$

and for the total work W done by the gas,

$$W = W_1 + W_2 - W_3 - W_4 = R (T_2 - T_1) \log_e \frac{V_2}{V_1}. \tag{44}$$

This result, viz., that $Q = W$, must of course be obtained, since, in any cyclic process (see equation (5), Chap. IV), the work done is equal to the heat absorbed.

Let us calculate the amount of work obtained compared with the quantity of heat absorbed at the temperature T_2. Since

$$W = R (T_2 - T_1) \log_e \frac{V_2}{V_1}$$

and

$$Q_2 = RT_2 \log_e \frac{V_2}{V_1},$$

we find

$$W = \frac{T_2 - T_1}{T_2} \cdot Q_2. \tag{45}$$

Using an ideal gas and carrying out a Carnot cycle in a reversible manner, we find that the amount of work obtained is a definite fraction $\frac{T_2 - T_1}{T_2}$ of the heat Q_2 absorbed at the higher temperature. The process is sometimes described by saying that a quantity of heat Q_2 at a higher temperature T_2 has been converted partly into work W and partly into heat Q_1 at a lower temperature T_1. Since we can reverse every stage of the Carnot cycle and starting at D (Fig. 9) describe the cycle $DCBAD$, we have in this process a means of taking a quantity of heat Q_1 from a reservoir at a temperature T_1 and, by doing a certain amount of work W, of delivering to a reservoir at the higher temperature T_2 the quantity of heat Q_2.

Although in the reversible Carnot Cycle, using an ideal gas, the quantity of work W is equal to a definite fraction $\frac{T_2 - T_1}{T_2}$ of the heat Q_2 absorbed at the higher temperature T_2, it does not follow that the same fraction would be obtained if the substance or system employed were not an ideal gas. As a matter of fact, the same fraction $\frac{T_2 - T_1}{T_2}$ is obtained, no matter what substance is employed. The proof, however, of this statement is based on the Second Law of Thermodynamics and until the Second Law is established we can take the results obtained above as holding only for ideal gases. An interesting deduction from equations (37) and (40) is that $\frac{Q_2}{T_2}$ is equal to $\frac{Q_1}{T_1}$, a relation the significance of which will be appreciated when we come to a study of the Second Law.

PROBLEMS

(Assume gases to be ideal)

1. What is the difference between c_p and c_v in the case of 1 gram of oxygen? carbon dioxide?

2. Calculate in calories, ergs and liter-atmospheres, the heat absorbed when 10 grams of hydrogen at 0° C. are expanded isothermally from an initial pressure of 16 atmospheres to a final pressure of 1 atmosphere. Calculate also the initial and final volumes.

3. A mass of helium is at 0° C. and 1 atmosphere. It is expanded adiabatically to a pressure of 0.05 atmosphere. What is its final temperature? Is it necessary to know the quantity of helium in solving this problem?

4. A quantity of air undergoes an adiabatic change from 10 atmospheres to 1 atmosphere. The original temperature was 17° C. Find the final temperature.

5. Ten liters of nitrogen at 27° C. are compressed adiabatically to a volume of two liters. Calculate the final temperature.

6. Eight grams of oxygen at 27° C. and a pressure of 1 atmosphere are compressed adiabatically to a final pressure of 16 atmospheres. Calculate the final volume and temperature.

7. Calculate the work done in the processes described in problems 3, 4, 5, 6, assuming that in the first three cases one mole of the gas is used.

8. Five liters of a gas at 27° C. are expanded adiabatically to a volume of 6.02 liters and a temperature of 5° C. Calculate the molecular heats at constant volume and constant pressure.

CHAPTER VI

APPLICATIONS OF THE FIRST LAW II THERMOCHEMISTRY

Heterogeneous Systems

A substance may exist in general as a gas, as a liquid or in one or more solid forms, depending on the pressure and temperature. We shall refer to these different forms as states of aggregation. The change from one form to another is ordinarily accompanied by considerable heat effects and sometimes by important volume changes. The heat absorbed during the isothermal fusion, sublimation or evaporation of unit mass of the substance under a constant pressure is called the latent heat of fusion, sublimation or evaporation. The term "latent" is applied because the process is so carried out that the absorption of heat does not effect any elevation in the temperature of the body. If u_1, v_1 and u_2, v_2 represent the energy and volume of one gram of the substance in the initial and final states respectively and if p is the constant pressure under which the process takes place, the heat q absorbed during the process is

$$q = u_2 - u_1 + p\,(v_2 - v_1). \qquad (1)$$

The term $u_2 - u_1$ measures the increase in the energy of the unit mass and the expression $p\,(v_2 - v_1)$ represents the external work done. The increase in energy $u_2 - u_1$ is often called the internal latent heat. If we represent by λ_f, λ_s and λ the latent heats of fusion, sublimation and evaporation of one gram of a substance and by λ_f', λ_s' and λ' the internal latent heats, we shall have three equations of the form

$$\lambda = \lambda' + p\,(v_2 - v_1). \qquad (2)$$

If we desire to deal with one mole of a substance, we shall use the symbols L_f, L_s and L to mean the molecular or molar latent

heats and V_2 and V_1 to stand for the molecular or molar volumes. For one mole of a substance we shall have, analogously to equation (2), three equations of the form

$$L = L' + p\,(V_2 - V_1). \tag{3}$$

Fusion

Applied to the case of fusion of a substance, equation (2) becomes

$$\lambda_f = \lambda_f' + p\,(v_2 - v_1), \tag{4}$$

in which v_2 and v_1 are the specific volumes of the liquid and solid respectively. Let us consider the special case of the fusion of ice at 0° C. at a pressure of one atmosphere and let us determine the relative importance of the two terms λ_f' and $p\,(v_2 - v_1)$ which together make up the total heat of fusion λ_f. In this case, $v_2 = 0.9999$ and $v_1 = 1.0908$. The value of $p\,(v_2 - v_1)$ when $p = 1$ atmosphere is therefore -0.0909 atmosphere-cc. Since 1 liter-atmosphere = 24.205 calories (Chap. IV), -0.0909 atmosphere-cc. $= \frac{-0.0909 \times 24.205}{1000} = -0.0022$ calories. Since the value of λ_f is 79.8 calories we see that the part due to the term $p\,(v_2 - v_1)$ is negligible. It is also true in general that in all processes in which only solids or liquids are concerned, the thermal value of the mechanical work due to the slight changes in the volume of the system is very small compared with the total energy change.

Evaporation

If we have the liquid and gaseous forms of a substance coexisting under the same pressure, namely, that of the vapor, we know by experience that this pressure (which we shall call the pressure of saturated vapor and represent by p_s) depends only on the temperature. By supplying heat to the system, a portion of the liquid will be transformed into vapor and the total volume of vapor will increase under the constant pressure p_s. If we consider the evaporation of one gram of the substance, we shall have

$$\lambda = q = u_2 - u_1 + p_s\,(v_2 - v_1), \tag{5}$$

where u_2, v_2 refer to the vapor, and u_1, v_1, to the liquid. Or we may write the equation as follows:

$$\lambda = \lambda' + p_s (v_2 - v_1), \tag{6}$$

or, in the case of one mole,

$$L = L' + p_s (V_2 - V_1). \tag{7}$$

Let us apply our equations to the case of water at 100° C. where p_s is 1 atmosphere. In this case λ is 538.8 calories, $v_2 = 1674$ cc., $v_1 = 1$ cc. and $p_s = 1$ atmosphere. The value of $p_s (v_2 - v_1)$ is then 1673 atmosphere-cc. = 40.5 calories. Hence λ', the internal heat of vaporization, is 498.3 calories. The value of the term $p (v_2 - v_1)$ is therefore in general not to be neglected in processes in which gases take part. An approximate determination of the value of $p_s (v_2 - v_1)$ can be easily made if we assume that water vapor follows the ideal gas laws. If M is the molecular weight of water vapor, then for 1 gram of the vapor we have the relation $p_s v_2 = \frac{R}{M} T$, in which R has the value of 1.987, if pv is to be converted into calories. In the case of water and water vapor at 100° C. we can set $p_s (v_2 - v_1)$ equal to $p_s v_2$ equal to $\frac{1.987}{18.02} \times 373$ and we obtain in this manner 41.1 calories instead of the more accurate value 40.5 obtained above.

Latent Heat of Sublimation

Let the symbols u_1, u_2, u_3, v_1, v_2, v_3 refer in order to one gram of the substance in the solid, liquid and vapor states respectively and let p_s and T_o be the pressure and temperature at which all co-exist. Then we have the following relations:

$$\text{heat of fusion} = \lambda_f = u_2 - u_1 + p_s (v_2 - v_1), \tag{8}$$

$$\text{heat of evaporation, } \lambda = u_3 - u_2 + p_s (v_3 - v_2), \tag{9}$$

$$\text{heat of sublimation, } \lambda_s = u_3 - u_1 + p_s (v_3 - v_1), \tag{10}$$

from which we deduce

$$\lambda_s = \lambda_f + \lambda \tag{11}$$

or the heat of sublimation is equal to the sum of the heats of fusion and evaporation at the same temperature. One point however needs to be considered. The value of λ_f the heat of fusion is usually given for a pressure of one atmosphere, and not the equilibrium pressure p_s. But since the value of $p(v_2 - v_1)$ is very small when applied to the process of fusion, a difference even of several atmospheres will not have any noticeable effect on the value of λ_f. Hence in equation (11), λ_f may refer to fusion at any moderate pressure, whereas λ_s and λ must refer to the same pressure. It is also understood that all three processes are to be carried out at temperatures which may be considered identical.

Thermochemistry

Thermochemistry in the widest sense has to do not merely with the changes in energy associated with chemical reactions but also with the relation between these energy changes and other properties of the system studied, the equilibrium constant, for instance. We shall however in this section deal exclusively with the application of the First Law to chemical changes and hence be content with a study of the various types of reactions and of the changes in energy accompanying them.

The most general statement of the First Law in its application to any process whatever, physical or chemical, is contained in the equation

$$Q = U_2 - U_1 + W. \qquad (12)$$

Now the value of $U_2 - U_1$ depends only on the initial and final states and is therefore independent of the way in which the system has gone from the initial to the final state. This is however not in general true of W, the work done by the system on the surroundings. Even in the case in which the external work is simply the mechanical work due to a change in volume against a pressure, i.e., when the mechanical work W is equal to $\int_{V_1}^{V_2} p\,dV$, the value of this integral depends not simply on the initial and final values of p and V, but also on the relation between them during the whole process. Let us illustrate this point by means of the diagram in Fig. 10.

Let the initial and final states of the system be represented by the points A and D respectively on the $p-V$ diagram. Let U_1 and U_2 be the initial and final values of the energy of the system. If the system proceeds from A to D through a series of intermediate states represented by the curve ABD, the mechanical work W is equal to $\int_{V_1}^{V_2} p\,dV$ and is given by the area under the curve, i.e., W = area $ABDFE$. If the process takes place in a different way, say along ACD, the work W is equal to the area $ACDFE$. It follows that the mechanical work done depends on the nature of the process as well as on the initial and final states and evidently, from the equation $Q = U_2 - U_1 + W$, the quantity of heat absorbed also depends on the intermediate steps in the process. In order that the work done and therefore the heat absorbed or evolved in any process shall be perfectly definite, we must so define the process that the value of the integral $\int_{V_1}^{V_2} p\,dV$ is the same, no matter how the system goes from its initial to its final state. The Law of Constant Heat Summation announced by Hess in 1840 is frequently stated as follows: The initial and final conditions alone determine the total heat evolved or absorbed in a reaction or series of successive reactions and the intermediate steps may be few or many but cannot alter the total heat effect. Stated in that manner, the law is false, but we can easily derive the correct formulation. The value of the integral $\int_{V_1}^{V_2} p\,dV$ will be perfectly definite and independent of the intermediate stages so long as either of the following conditions holds throughout the process; the external pressure on the system must be constant throughout the whole series of changes or the total volume of the system must remain unchanged. In the first case the work W is equal to $p\,(V_2 - V_1)$, an expression whose value

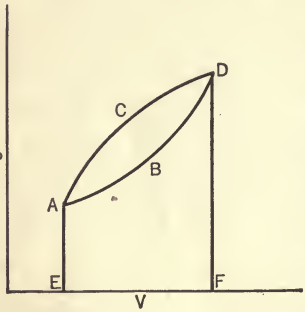


FIG. 10

depends only on the initial and final states; in the second case, since dV is zero, the value of the integral is zero. We can therefore restate the Law of Hess in the following manner. The quantity of heat absorbed or evolved when a system goes from one state to another is independent of the nature of the intermediate stages so long as the whole process is carried out either at constant pressure or constant volume.

Exothermal and Endothermal Processes

We have been speaking of reactions in which heat is either absorbed or liberated without specifying clearly what is meant by these expressions. If in order to restore the system to its original temperature heat must be given off to the surroundings, we shall say that the reaction liberates or evolves heat and shall call it an exothermal reaction. If in order to restore the system to its original temperature, heat must flow in from the surroundings, we shall say that the reaction absorbs heat and shall describe it as an endothermal reaction.

Energy of a Mixture of Gases

If communication is established between two vessels containing different gases at the same temperature T, so that diffusion takes place without any external work being done, the mixture of gases is observed to have virtually the same temperature as each of the original gases. Since the gases have done no work on the surroundings and since there has been no heat exchange, the mixture of gases has an amount of energy equal to the sum of the energies of the original gases. We shall suppose that this result is strictly true for ideal gases, since it is sufficiently exact for actual gases. Thus we can suppose that the energy of each gas in a mixture of gases is the same as if the gas were in the pure state and at the same temperature as the mixture. The total energy of a mixture of ideal gases depends only on the temperature and is independent of the volume or pressure.

Gaseous Reactions

We shall adopt the following scheme of representing a chemical change between gases,

$$\nu_1 A_1 + \cdots = \nu_2 A_2 + \cdots \tag{13}$$

in which A_1 is the molecular formula of one of the initial substances and ν_1 is the number of moles of A_1 which disappear in the course of the reaction. Similarly A_2 is one of the substances formed in the reaction and ν_2 the number of moles of it that are produced. We shall adopt the convention of considering ν_2 and similar coefficients as positive and ν_1 and similar coefficients as negative, so that the expression $\sum \nu$ shall mean the increase in the number of moles in the course of the reaction. Thus in the case of the union of hydrogen and oxygen to form water vapor, represented by the equation $2\ H_2 + O_2 = 2\ H_2O$, the coefficients on the left hand side are to be taken as negative, while that on the right is to be taken as positive, so that $\sum \nu$ in this case is equal to $-2 - 1 + 2 = -1$. If we are considering the dissociation of water vapor into hydrogen and oxygen, we shall write the equation $2\ H_2O = 2\ H_2 + O_2$ and in this case $\sum \nu$ is equal to $-2 + 2 + 1 = 1$.

Reactions at Constant Pressure

For any process in which the pressure is maintained constant throughout and in which the only form of work is that due to the change in volume of the system, the value of this external work W is

$$W = p\,(V_2 - V_1). \tag{14}$$

Accordingly Q, the heat absorbed, is

$$Q = U_2 - U_1 + p\,(V_2 - V_1). \tag{15}$$

Since in most works on thermochemistry it is customary to consider heat evolved as positive and heat absorbed as negative, we shall use the symbol H_p to stand for the heat evolved at constant pressure when the final system is restored to its original temperature and when the total work done is purely mechanical and therefore equal to $p\,(V_2 - V_1)$. For such reactions then

$$H_p = U_1 - U_2 - p\,(V_2 - V_1). \tag{16}$$

This may be written as follows:

$$H_p = (U + pV)_1 - (U + pV)_2, \tag{17}$$

which indicates that H_p measures the decrease in the value of the function $(U + pV)$ frequently called the heat-function at constant pressure. If the same gaseous reaction is carried out at the same temperature, but at constant volume V_1, the heat evolved at constant volume, represented by H_v, will be

$$H_v = U_1 - U_2. \tag{18}$$

Now it is to be borne in mind that though the U_1 of equation (18) is identical with the U_1 of equation (16), this is not in general true of U_2. The U_2 of equation (18) refers to a total volume of the system equal to V_1, the U_2 of equation (16) refers to a volume V_2. In the case of gases, U_2 is essentially the same in both cases, since the energy of ideal gases does not depend on their volume. In the case of liquids and solids, the energy does depend on the volume and hence the value of U_2 would be different in the two cases. If we are dealing with gases, we can therefore write

$$H_p = H_v - p\,(V_2 - V_1). \tag{19}$$

Now if in any gaseous reaction such as is represented by equation (13), the total number of moles originally is n_1 and finally n_2, we have $\sum\nu = n_2 - n_1$. Also if the pressure is constant throughout the reaction, $pV_1 = n_1RT$ and $pV_2 = n_2RT$. Hence

$$p\,(V_2 - V_1) = (n_2 - n_1)\,RT = \sum\nu RT,$$

and we can write equation (19) in the simpler form,

$$H_v = H_p + \sum\nu RT. \tag{20}$$

This equation is valid only for reactions between gases. If the values of H_v and H_p are expressed in calories, the value of R is 1.987. Since the term $\sum\nu RT$ is frequently much smaller than H_p, it will be evident that no appreciable error will in general be made if we take the numerical value of R as 2. Under these circumstances equation (20) becomes

$$H_v = H_p + \sum\nu \cdot 2\,T. \tag{21}$$

Reactions in Heterogeneous Systems

Unless both the initial and final states of a system include a gaseous phase, it is usually inconvenient or even impossible to carry out a reaction at a given temperature and maintain the volume strictly constant. Thus if we consider the freezing of water at 0° C. it is impossible to carry out this process at constant volume. Such processes can however be carried out without doing external work, e.g., by having the reaction take place in a closed vessel which is sufficiently large and which may or may not contain an indifferent gas. Under these circumstances the process proceeds practically under constant pressure without however furnishing any mechanical work to the surroundings. In the case of reactions in heterogeneous as well as in gaseous systems we shall define H_v by equation (19); viz.: $H_v = H_p + p(V_2 - V_1)$; i.e., H_v is equal to the heat H_p liberated at constant pressure plus the thermal equivalent of the mechanical work. H_v measures therefore the decrease in the energy of the system when the process takes place at constant pressure. Unless otherwise specified, when we speak of the heat evolved in a reaction we shall refer to H_p, the heat liberated at constant pressure. Since the energy of a substance depends on its state of aggregation, this must be indicated in some way when there is any possibility of doubt as to the state of aggregation. Since most thermochemical data refer to reactions at room temperature, this is the temperature to be assumed unless otherwise expressly stated. To distinguish the different states of aggregation, the formulas of solids may be enclosed in square brackets and those of gases in curved parentheses, while the formulas of substances in the liquid state are written without brackets. Thus the symbols $[H_2O]$, H_2O and (H_2O) would refer to one mole of ice, liquid water and water vapor respectively. Most of our thermochemical data are taken from Landolt-Börnstein Tabellen (1912) and are based principally on the extensive researches of Julius Thomsen and Berthelot.

Thermochemical Equations

Equation (13) indicates the material changes that occur in a reaction, but does not say anything about the thermal changes. The heat effect of a reaction may be specified in the following way:

$$\nu_1 A_1 + \cdots = \nu_2 A_2 + \cdots + H_p \qquad (22)$$

for reactions at constant pressure. Thus the equation, $(H_2) + (Cl_2) = 2\,(HCl) + 44{,}000$ calories, gives 44,000 calories as the heat evolved on the union of 1 mole of hydrogen and 1 mole of chlorine, room temperature and constant pressure being presumed. All our thermochemical equations will refer to constant pressure; the value of H_v can be calculated if desired from H_p by using equations (19), (20) or (21). If we adopt the convention that in a thermochemical equation, the symbol (H_2) for example shall stand for the value of the heat function, $U + pV$, possessed by 1 mole of hydrogen, then the equation we have just been considering is thermochemically equivalent to $(U + pV)_{H_2} + (U + pV)_{Cl_2} = (U + pV)_{2\,HCl} + 44{,}000$ calories. Now the terms on the left are the total value of $U + pV$ in the initial state, that is, $(U + pV)_1$, whereas $(U + pV)_{2\,HCl}$ is the final value or $(U + pV)_2$, hence, considered as a mathematical equation, we have $(U + pV)_1 - (U + pV)_2 = 44{,}000$ calories and this according to equation (17) is equal to H_p. Since the absolute values of the heat function $U + pV$ are not known (the same is true of the function U, the energy) and since we are concerned only with differences in the value of these functions, we can adopt arbitrarily any convenient state as one that shall possess zero value of the function $U + pV$. We shall therefore simplify many of our calculations by assuming that the elements in the state and at the temperature in which they enter into any given reaction possess zero value of the heat function. Writing the values of this function in the above equation, we should necessarily have

$$\begin{array}{ccccc} (H_2) & + & (Cl_2) & = & 2\,(HCl) + 44{,}000 \text{ cal.} \\ 0 & & 0 & & -44{,}000. \end{array} \qquad (23)$$

In this case, when we have a compound formed from its elements, the heat evolved at constant pressure during the process will be

called the *heat of formation* of the compound. Thus the heat of formation of two moles of HCl gas is 44,000 calories. Since the value of the heat function $U + pV$ for two moles, according to equation (23), is $-44{,}000$ calories (supposing the values for the elements H_2 and Cl_2 to be zero), we deduce the following rule: the value of the heat function for a mole of a compound is equal to the heat of formation of a mole of the compound with the sign changed. We can illustrate the usefulness of this convention by calculating the heat of formation of acetylene from its heat of combustion and the heats of formation of CO_2 and liquid H_2O. The heat of formation of CO_2 is 96,960 calories, that of 1 mole of H_2O as liquid is 68,400. The heat of combustion of 1 mole of C_2H_2 is 310,050. If x is the heat of formation of 1 mole of acetylene, we obtain from the equation,

$$\begin{aligned}(C_2H_2) + \tfrac{5}{2}(O_2) &= 2\,(CO_2) + H_2O + H_p \\ -x \quad +0 \quad &= -2 \times 96{,}960 - 68{,}400 + 310{,}050,\end{aligned}$$

the heat of formation, x, of one mole of acetylene as $-47{,}730$ calories. On this account acetylene is often called an endothermic compound.

In many cases it is desired to know the heat effect of a process which either cannot be carried out directly or at least cannot be studied free from side reactions. This will be illustrated by calculating the heat evolved at constant pressure when 12 grams of amorphous carbon are burned in oxygen to form carbon monoxide. We are unable to burn carbon directly to carbon monoxide without producing some carbon dioxide, so that the direct experimental determination of the heat effect that we wish to measure is impossible. The heat effect can however be obtained as follows. The heats of combustion of carbon to CO_2 and of CO to CO_2 are known. Thus we have the thermochemical equations

$$[C] + (O_2) = (CO_2) + 96{,}960 \text{ cal.}$$
$$(CO) + \tfrac{1}{2}(O_2) = (CO_2) + 67{,}960 \text{ cal.}$$

Subtracting the second equation from the first and rearranging, we obtain

$$[C] + \tfrac{1}{2}(O_2) = (CO) + 29{,}000 \text{ cal.}$$

We shall also calculate the heat effect of this reaction by the same method as was employed above in calculating the heat of formation of acetylene. Since the heat of formation of CO_2 is 96,960, we have the following relation:

$$\begin{aligned} CO + \tfrac{1}{2}(O_2) &= CO_2 + H_p \\ -x + 0 &= -96{,}960 + 67{,}960 \end{aligned}$$

whence x, the heat of formation of CO, is 29,000 calories.

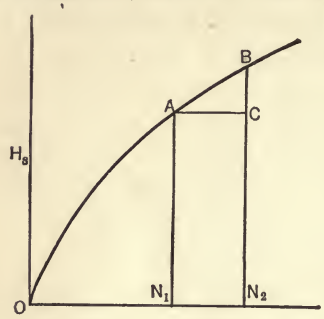
Heats of Solution and Dilution

The formation of a liquid solution is usually accompanied by a noticeable evolution or absorption of heat. Thus if solid KNO_3 is dissolved in water, the solution will absorb heat from the surroundings; if solid NaOH is dissolved in water, the solution will give off heat to the surroundings. The quantity of heat liberated or absorbed when one mole of a substance is dissolved in n moles of a solvent we shall call the integral heat of solution and represent by H_s. The value of H_s depends on n or $H_s = f(n)$. It is an empirical fact that for sufficiently large values of n, addition of more solvent produces no heat effect. An aqueous solution of KNO_3 for which this is true will be represented by KNO_3Aq. If H_d represents the heat of dilution of a solution containing one mole of solute, we evidently have the relation $H_d = (H_s)_{n_2} - (H_s)_{n_1}$ which means that if to a solution containing n_1 moles of solvent we add $(n_2 - n_1)$ moles of solvent the heat evolved is

$$(H_s)_{n_2} - (H_s)_{n_1} \quad \text{or} \quad f(n_2) - f(n_1).$$

Since $\dfrac{dH_s}{dn} = \dfrac{df(n)}{dn}$ or $dH_s = \dfrac{df(n)}{dn}\,dn$, dH_s is the heat evolved on adding dn moles of solvent to a solution consisting of one mole of solute and n moles of solvent. The addition of this infinitesimal amount of solvent does not change the composition of the solution. We can express our results in the following way: if we add one mole of solvent to an infinite amount of solution consisting of one mole of solute to n moles of solvent, the heat of dilution is equal to $\dfrac{df(n)}{dn}$. This is called the differential heat of dilution.

Although we have distinguished the two components as solute and solvent, that has been done merely for the sake of convenience. Thus in a mixture of water and H_2SO_4, either component may be looked on as the solvent. The results may be represented diagrammatically in the accompanying Fig. 11.



N moles of B to 1 mole of A

FIG. 11

The ordinate at A is the heat of solution of one mole of A in n_1 moles of B. BC is the integral heat of dilution when B is increased from n_1 to n_2. The tangent to the curve at A will represent the differential heat of dilution of a solution containing n_1 moles of B.

Heat of Neutralization

Another important heat effect is that obtained by the interaction of aqueous solutions of acids and bases. The heat of neutralization in very dilute solutions will be represented as in the following example:

$$NaOHAq + HClAq = NaClAq + H_2O + 13{,}700 \text{ cal.}$$

It may be mentioned at this point that Thomsen and other investigators have found that the neutralization of one equivalent of an active acid (such as HCl, HNO_3, HBr, etc.) by an active base (such as NaOH, KOH, $Ba(OH)_2$, etc.) always liberates approximately 13,700 calories. As early as Hess, it was also found experimentally, that the mixing of dilute solutions of salts does not produce any heat effect provided there is no precipitation. The significance of these two generalizations from the standpoint of the modern theory of ionization of aqueous salt solutions cannot however be dwelt on in this place.

Effect of Temperature on Heats of Reaction

So far we have considered the heat effects that are produced in a given process at one temperature only. In this section we

shall see if there is any connection between the heat effects of a given reaction at different temperatures. The connection can be readily deduced in the following manner. For any system to which heat is added, we have $Q = dU + pdV$. If the quantity of heat is so small that it produces only an infinitely small rise in temperature dT, the ratio $\frac{Q}{dT}$ is called the heat capacity C of the system or

$$C = \frac{Q}{dT} = \frac{dU}{dT} + p\frac{dV}{dT}. \tag{24}$$

In the case of an elevation at constant pressure, the heat capacity C_p is evidently given by the equation

$$C_p = \left(\frac{d(U + pV)}{dT}\right)_p. \tag{25}$$

Now since $H_p = (U + pV)_1 - (U + pV)_2$, we find

$$\left(\frac{dH_p}{dT}\right)_p = \left[\frac{d(U + pV)_1}{dT}\right]_p - \left[\frac{d(U + pV)_2}{dT}\right]_p, \tag{26}$$

and therefore from equation (25)

$$\left(\frac{dH_p}{dT}\right)_p = (C_1 - C_2)_p. \tag{27}$$

We may write equation (27) in the form,

$$dH_p = (C_1 - C_2)_p\, dT. \tag{28}$$

If, dropping the subscript p, H_2 and H_1 are the values of H_p at the temperatures T_2 and T_1, we obtain on integrating (28)

$$H_2 - H_1 = \int_{T_1}^{T_2} (C_1 - C_2)_p\, dT \tag{29}$$

If the heat capacities of the system are known as functions of the temperature, the integral in (29) can be evaluated. In many cases, we can suppose the heat capacities to be constant over a small interval $(T_2 - T_1)$ of temperature. With this supposition equation (29) becomes

$$H_2 - H_1 = (C_1 - C_2)_p\,(T_2 - T_1) \tag{30}$$

This may be written in the more compact form,

$$\Delta H_p = (C_1 - C_2)_p \Delta T$$

where ΔH_p and ΔT refer to finite increases in the values of H_p and T. These results were first deduced by Kirchhoff. They can also be obtained by a consideration of a cyclic process as represented in Fig. 11a.

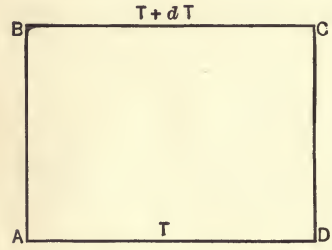


FIG. 11a

In this figure let A and D represent the initial and final states of a system at the temperature T and pressure p and let B and C have the same significance for $T + dT$ and the same pressure p. Also for the sake of convenience let the letters A, B, C, and D represent the values of the function $U + pV$ in the four states mentioned. Let C_1 and C_2 be the heat capacities of the initial and final states at the constant pressure p. We shall imagine our system to go from A to D in two ways: first directly at the temperature T; secondly along the lines AB, BC and CD. If H_{T+dT} and H_T represent the heat evolved at constant pressure when the reaction takes place at the temperatures $T + dT$ and T, respectively, evidently

$$H_{T+dT} = B - C \quad \text{and} \quad H_T = A - D. \tag{31}$$

But since the states B and C are reached by raising the temperature of the systems A and D respectively by dT,

$$B = A + C_1 dT \quad \text{and} \quad C = D + C_2 dT. \tag{32}$$

From equation (31), we have

$$H_{T+dT} - H_T = dH_p = B - C - A + D$$

and from the equations (32)

$$H_{T+dT} - H_T = dH_p = (C_1 - C_2)\, dT \tag{33}$$

which is identical with equation (28) obtained previously.

As an application of Kirchhoff's equation, let us determine how the heat of combustion of hydrogen and oxygen to form liquid

water varies with the temperature. At room temperature and constant pressure, we have

$$(H_2) + \tfrac{1}{2}(O_2) = H_2O + 68{,}400 \text{ cal.}$$

C_1 the heat capacity at constant pressure of 1 mole of hydrogen and $\frac{1}{2}$ mole of oxygen is (Table IX, Chap. V) $6.87 + \frac{1}{2} \times 6.96 = 10.35$. C_2, the heat capacity of 1 mole of water, is 18. Hence, applying equation (28), $dH_p = -7.65\, dT$. Assuming the heat capacities to be constant over a moderate range of temperature, this result may be stated as follows: the heat of combustion of 1 mole of hydrogen to form liquid water decreases by 7.65 calories when the temperature at which the reaction is carried out is increased by one degree.

The "Principle" of Thomsen and Berthelot

Both Thomsen and Berthelot saw in the heat evolved in reactions a measure of the driving force tending to make the reaction go in a certain direction. They were led to enunciate a principle, very curiously named the principle of maximum work by Berthelot, according to which if a number of substances are brought together that reaction will take place which evolves the greatest amount of heat. The erroneousness of this principle can be shown by a simple example. If one introduces the three substances PCl_5, PCl_3 and Cl_2 into a vessel, a reaction will in general take place, but the direction is determined by the temperature and concentrations of the substances and not by the heat evolved. It is perhaps true to say that the majority of the common reactions at ordinary temperatures are exothermic but there is no ground for considering that the law of Thomsen and Berthelot is anything more than a very incomplete and often erroneous statement of facts.

The following tables contain representative selections from the mass of thermochemical data. In all cases, the figures refer to the heat effect at constant pressure and at room temperature. Also, unless otherwise specified, the various substances are to be assumed to be in the state of aggregation corresponding to room temperature and a pressure of one atmosphere.

I. Compounds of Metals. Heats of Formation

(a) Oxides

Na_2O	Approx. 100,000
K_2O	" 100,000
CaO	" 145,000
BaO	" 130,000
MgO	143,600
ZnO	85,440
FeO	65,700
Fe_2O_3	197,000
Fe_3O_4	270,800
NiO	57,900
PbO	50,300
Cu_2O	40,800
CuO	37,200
Ag_2O	5,900–7,000
Hg_2O	22,200
HgO	21,500

(b) Sulphides

Na_2S	89,300
K_2S	103,500
CaS	90,800
BaS	102,500
CuS	10,000
Ag_2S	3,300
PbS	18,400

(c) Chlorides

$NaCl$	97,700
KCl	105,600
$BaCl_2$	196,900
$MgCl_2$	151,000
$ZnCl_2$	97,200
$FeCl_2$	82,050
$FeCl_3$	96,040
$NiCl_2$	74,530
$CuCl$	32,900
$CuCl_2$	51,630
$AgCl$	29,900
$HgCl$	31,300
$HgCl_2$	53,300
$PbCl_2$	82,800

(d) Bromides

$NaBr$	85,700
KBr	95,300
$CuBr_2$	32,600
$CuBr$	24,980
$AgBr$	22,700
$PbBr_2$	64,450

(e) Iodides

NaI	69,100
KI	80,130
CuI	16,300
AgI	15,000
PbI_2	39,800

(f) Nitrates

$NaNO_3$	111,000
KNO_3	119,000
$Ba(NO_3)_2$	228,000
$AgNO_3$	28,740
$Pb(NO_3)_2$	105,500

(g) Sulphates

Na_2SO_4	328,590
K_2SO_4	344,300
$BaSO_4$	340,000
$MgSO_4$	302,000
$ZnSO_4$	229,600
$CuSO_4$	182,600
Ag_2SO_4	167,300
$PbSO_4$	216,210

II. Heats of Formation, Compounds of Non-Metals

HCl	22,000
HBr	8,440
HI	−6,040
H_2O (liq.)	68,360
H_2O (gas)	58,000
H_2S	2,730
NH_3	11,890
SO_2	71,080
SO_3 (liq.)	103,240
H_2SO_4	192,920
N_2O	−17,740
NO	−21,570
HNO_3	41,600
CO (amorphous carb.)	29,000
CO_2 " "	96,960
CH_4 " "	21,750
C_2H_6	28,560
C_2H_4	− 2,710
C_2H_2	−47,770
C_6H_6	−12,510

III. HEATS OF SOLUTION

Substance	Moles H_2O	H_p	Substance	Moles H_2O	H_p
HCl	300	17,315	NaBr	200	− 190
HBr	400	19,940	$NaBr.2H_2O$	300	− 4,710
HI	500	19,210	NaI	200	+ 1,220
NH_3	200	8,430	$NaI.2H_2O$	300	− 4,010
SO_2	250	7,700	NaOH	200	+ 9,940
SO_3 (liq.)	1600	39,170	$NaNO_3$	200	− 5,030
H_2SO_4	1600	17,850	Na_2SO_4	400	+ 460
HNO_3	300	7,480	$Na_2SO_4.10H_2O$	400	−18,760
$HC_2H_3O_2$	200	375	KCl	200	− 4,440
NH_4Cl	200	− 3,880	KBr	200	− 5,080
NH_4Br	200	− 4,380	KI	200	− 5,110
NH_4I	200	− 3,550	KOH	250	+13,290
NH_4NO_3	200	− 6,320	KNO_3	200	− 8,520
$(NH_4)_2SO_4$	400	− 2,370	K_2SO_4	400	− 6,380
NaCl	100	− 1,180	$Ba(OH)_2$	....	+12,260
$Ca(OH)_2$	2500	+ 2,790	$BaCl_2$	400	+ 2,070
$CaCl_2$	300	+17,410	$BaCl_2.2H_2O$	400	− 4,980
$CaCl_2.6H_2O$	400	− 4,310	$CuSO_4$	400	+15,800
$ZnCl_2$	300	+15,630	$CuSO_4.5H_2O$	400	− 2,750
$ZnSO_4.7H_2O$	400	− 4,260	$Cu(NO_3)_2.6H_2O$	400	−10,710
$ZnSO_4$	400	+18,430	$PbCl_2$	1800	− 6,800
$FeCl_2$	350	+17,900	$PbBr_2$	2500	−10,040
$CuCl_2$	600	+11,080	$Pb(NO_3)_2$	400	− 7,610
$CuCl_2.2H_2O$	400	+ 4,210	$AgNO_3$	200	− 5,440
			Ag_2SO_4	1400	− 4,480

IV. HEATS OF COMBUSTION AT CONSTANT PRESSURE AND ROOM TEMPERATURE

(the product water being liquid)

CH_4	211,930	C_2H_5OH (liq.)	327,000
C_2H_6	370,440	n-C_3H_7OH (vapor)	498,600
C_3H_8	529,210	n-C_3H_7OH (liq.)	480,800
C_6H_6 (vap.)	799,350	$(CH_3)_2O$	349,360
C_2H_4	333,350	$(C_2H_5)_2O$ (vap.)	659,600
C_2H_2	310,050	$(C_2H_5)_2O$ (liq.)	652,300
CH_3OH (vap.)	182,230	$C_{12}H_{22}O_{11}$ (cane sugar)	1,355,000
CH_3OH (liq.)	170,000	$C_6H_5CO_2H$	772,800
C_2H_5OH (vapor)	340,530		

V. HEATS OF NEUTRALIZATION. (Base and Acid Approximately 0.28 Normal before Neutralization)

Base	HClAq	HFAq	HNO_3Aq	H_2SO_4Aq	$HC_2H_3O_2$
NaOHAq.....	13,780	16,270	13,680	31,380	13,400
LiOHAq.....	13,848	16,400	.....	31,288	.....
KOHAq.....	13,750	16,100	13,770	31,288	13,215
$Ba(OH)_2Aq$.....	27,780	32,300	28,260	36,900	26,900
				$BaSO_4$ ppted.	
$Ca(OH)_2Aq$.....	27,900	.....	.....	31,140	.....
$Sr(OH)_2Aq$.....	27,630	.....	.....	30,710	.....
NH_4OHAq.....	12,270	15,200	12,320	28,152	12,010
CH_3NH_2Aq.....	13,115	.....	.....	.....	.....
$(CH_3)_2NHAq$.....	11,810	.....	.....	.....	.....
$(CH_3)_3NAq$.....	8,740	.....	.....	21,080	.....
$(CH_3)_4NOHAq$....	13,750	.....	.....	31,032	.....
$(C_2H_5)_3SOHAq$...	13,720	.....	.....	30,590	.....

VI. HEATS OF NEUTRALIZATION AT DIFFERENT TEMPERATURES (WÖRMANN)

Temperature, ° C.	Concentration of acid and base, Normal	KOH + HCl	NaOH + HCl
0	0.5	14,805	14,984 $\left(\frac{N}{1}\right)$
0	0.25	14,707	14,580
0	0.10	14,709	14,604
6	0.25	14,473	14,352
6	0.1875	14,463	14,359
6	0.125	14,448	14,331
18	0.25	13,937	13,714
18	0.125	13,957	13,693
18	0.05	13,887	13,631
32	0.25	13,155	12,974
32	0.125	13,171	12,922
32	0.05	13,160	12,980

PROBLEMS

1. If the latent heat of sublimation of 1 gram of solid iodine at room temperature is 42.92 calories, calculate the heat of formation from the elements as gases: (1) of HI as a gas, (2) of HI in dilute solution.

2. The heat of formation of glycerol ($C_3H_5(OH)_3$) being 160,900 calories, calculate the heat of combustion.

3. Calculate the heat of the reaction $2\,Na + MgCl_2 = 2\,NaCl + Mg$, all the substances being solids.

4. Calculate the heat effect of the reaction $Zn + 2\,AgCl + 300\,H_2O = 2\,Ag + (ZnCl_2 + 300\,H_2O)$.

5. Calculate the difference in H_v and H_p for the following reactions:

(*a*) Combustion of acetylene at 18° C.; (*b*) Combustion of acetylene at 200° C.; (*c*) Combustion of hydrogen at 700° C.; (*d*) Dissociation of ammonia at 400° C.

6. The heat of solution of H_2SO_4 in n moles of water is given by Thomsen as equal to $\frac{17{,}860\,n}{n + 1.798}$. Calculate the heat of solution of 1 mole of H_2SO_4 in (*a*) 2 moles of water, (*b*) 10 moles of water. Calculate the heat evolved in adding 10 moles of water to a mixture of 1 mole of H_2SO_4 and 10 moles of water.

7. From the formula of problem (**6**) calculate the differential heat of dilution for a mixture containing 1 mole of H_2SO_4 and (*a*) 1 mole of water (*b*) 5 moles of water, (*c*) 20 moles of water, (*d*) 200 moles of water.

8. Calculate the heat evolved in adding 1 mole of H_2SO_4 to a mixture whose composition is (*a*) 1 mole of H_2SO_4 and 10 moles of water, (*b*) 1 mole of H_2SO_4 and 5 moles of water.

9. Calculate the difference in energy between 1 mole of liquid water at 0° C. and 1 atmosphere and 1 mole of water vapor at 100° C. and 1 atmosphere, taking the latent heat of vaporization of 1 gram of water at 100° C. to 538.7 calories and assuming the water vapor to be an ideal gas.

10. Solutions of the following composition, viz., $NaOH + 100\,H_2O$, $HCl + 100\,H_2O$, $NaCl + 201\,H_2O$ have the specific heats 0.968, 0.964 and 0.978 respectively. If the heat evolved on mixing the first two solutions at 10° C. is 14,253 calories, calculate the heat of neutralization at 18° C. and at 25° C.

11. The heat of solution of 1 mole of HCl in n moles of water is equal to $17{,}355 - \frac{11{,}980}{n}$ according to Thomsen. Calculate the heat of solution when $n = 1, 5, 10, \infty$. Calculate the heat of dilution from $n = 1$ to $n = 2$; from $n = 2$ to $n = 3$. Calculate the differential heat of dilution when $n = 1$, 2, 3, 10 and 100.

12. The heat of solution of 1 mole of NH_4NO_3 in n moles of water at 18° C.

is, according to Thomsen, equal to $-6410\left(\frac{n+2.424}{n+6}\right)$. The solution saturated at 18° C. consists of 1 mole of NH_4NO_3 and 2.48 moles of water. Calculate the heat of solution in 2.48, 5, 100, 200 and ∞ moles of water. Calculate the differential heat of dilution when $n = 2.48$, 5, 100 and 200. Calculate the heat effect when 1 mole of NH_4NO_3 dissolves in an infinite amount of a nearly saturated solution.

CHAPTER VII

THE SECOND LAW OF THERMODYNAMICS

If a given system can exist in two states which we shall designate as A and B, the First Law tells us that the difference in the energy of the system in the two states is a constant quantity. This difference may be positive, zero or negative. But if we raise the question as to whether state A will spontaneously change into state B or whether the reverse will occur, the First Law is unable to give any answer. This is evidenced also by the fact that all the relationships between two states of a system deduced from the First Law are given in the form of equations, no matter how the system may have gone from state A to state B, so that from the point of view of the First Law all possible states of a system are in a certain sense equivalent. If we are to find any way of predicting the direction of reactions, we must find some property of the system which always changes in a definite manner (for example, increases) when a process takes place spontaneously. And just as the statement of the First Law is an expression of the experience of mankind, so also we must go to experience if we desire to ascertain the conditions which determine the direction of natural processes. When we speak of a process as occurring spontaneously, we shall mean that the process will take place without any exchange of energy with the surroundings being necessary. In many spontaneous processes heat may for example be given off to the surroundings, but that is a result of the spontaneous process rather than a necessary accompaniment. The process would take place if the exchange of energy with the surroundings were prevented. We must therefore find out from experience what processes in Nature are spontaneous and what are their characteristics. In no other way can we hope to determine the direction of reactions than by an appeal to the experience of mankind. Thomsen and Berthelot indeed based their

law on experiment, for they had found in their experience that chemical reactions occur spontaneously accompanied by the evolution of heat. Now if this were the universal experience, we should have here the answer to our question. But as a matter of fact, Thomsen and Berthelot were either ignorant of or overlooked many reactions which occur spontaneously and absorb heat and as we pointed out at the close of the last chapter the principle of Thomsen and Berthelot is not of general application. Since we are desirous of finding a perfectly general criterion, we must not restrict our considerations to chemical reactions, but must include what are usually termed physical processes. Suppose we make a list of some of the different types of processes which we know will take place spontaneously. We shall have, among others, the flow of heat from a warmer to a colder body, the diffusion of gases into each other, the expansion of a gas into a vacuum, the crystallization of a salt from a supersaturated solution, the freezing of an undercooled liquid, the equalization of the temperature differences of bodies in a closed vessel by radiation, and finally any number of chemical reactions (as ordinarily carried out) when they proceed with a finite velocity. Now all these processes can be imagined to take place in a closed rigid vessel, impermeable to heat or any other form of energy, so that in each case we shall have an isolated system and the total energy of the system will not have changed. Nevertheless the process will have occurred. In an attempt to determine the nature of these spontaneous processes, let us see under what conditions we can reverse them.

Let us consider first of all the expansion of an ideal gas into a vacuum, a process which takes place spontaneously without any permanent change in temperature, without any exchange of heat or work with the surroundings and therefore without any change in the energy of the gas. Let us call the original and final states A and B. If we desire to return to state A, we may compress the gas to its original volume and then we may restore it to its original temperature by allowing a certain quantity of heat equivalent to the work done on the gas during the compression to flow into a heat reservoir. The gas is in its original state, but certain

weights which may have been used in the compression are at a lower level and also a heat reservoir has an additional quantity of heat. The original state everywhere can only be realized if it is possible to take the quantity of heat from the reservoir and convert it into its equivalent amount of work by raising the weights to their original position without causing any other changes whatsoever. Whether this is possible or not will be considered shortly.

Let us next consider the flow of heat from a warmer to a colder body. In state A, we have two bodies, the first at a temperature T_1 and the second at a higher temperature T_2. After a certain time, a finite quantity of heat will have gone from the second to the first. To simplify matters we shall suppose that the bodies are so large that the transfer of the quantity of heat Q does not appreciably change the temperatures of the bodies. In order to get back to state A, we must extract the quantity of heat Q from the body at the temperature T_1 and deliver it to the body at the higher temperature T_2 without producing any permanent change anywhere else. Now by means of the reversed Carnot cycle (see end of Chap. V), using an ideal gas, we can take the quantity of heat Q from a body at a temperature T_1 and by doing a certain amount of work W deliver to the body at the higher temperature T_2, the quantity of heat $Q + W$. This extra amount of heat equivalent to W may then be given isothermally by the body to a heat reservoir. Our two bodies are now in their original state, but a certain heat reservoir has an additional amount of heat W and also certain weights (which furnished the mechanical work) are at a lower level. All that remains to be done is to extract a quantity of heat W from the heat reservoir and to raise the weights to their original position and cause no change in anything anywhere else. We are thus face to face with the same problem as when we attempted to reverse the expansion of a gas into a vacuum.

We shall consider one more process, a chemical one, namely the interaction of zinc and an aqueous solution of copper sulphate, represented by the equation

$$\mathrm{Zn} + \mathrm{CuSO_4, Aq} = \mathrm{ZnSO_4, Aq} + \mathrm{Cu}.$$

In state A, we have 65.4 grams of zinc and the equivalent amount of a solution of copper sulphate at a certain temperature T. On bringing the zinc and the solution into contact, we obtain 63.6 grams of copper and a solution of zinc sulphate, and in addition the temperature of the system will be a number of degrees higher than it originally was. Can we restore everywhere state A? By means of a definite amount of electrical energy E making the copper one of the electrodes and a piece of zinc or any indifferent metal the other electrode, we can regain our 65.4 grams of zinc and the equivalent amount of copper sulphate. The system is however at a higher temperature than it was at originally and can give off the quantity of heat Q to a reservoir in cooling to its original state. From the First Law, $Q = E$. The electrical energy can be obtained in principle from the equivalent amount of mechanical work W. Everything will be in its original state if we can now take the quantity of heat Q from the reservoir and convert it into the mechanical work W without bringing about any changes whatever anywhere else.

The possibility of the conversion of heat into an equivalent amount of work without effecting other changes is undoubtedly a matter of the greatest importance. To use a time-honored illustration, the ocean has immense stores of energy and can give this energy up in the form of heat. If this heat could be converted into work as we have supposed, ocean-going vessels would no longer need to carry large amounts of coal or oil. Such a transformation of heat into its equivalent amount of work is not in any way contrary to the First Law and any machine which would enable this transformation to be effected would not be the kind of perpetual motion machine the possibility of which is denied by the First Law. It would however be almost as useful to mankind, for the work done in driving the ship would be restored in its entirety to the sea through friction, if we disregard the slight change in the potential energy of the ship in different parts of the world due to the fact that the earth's surface is not spherical. Ostwald has called such a machine a perpetual motion machine of the second kind.

In order that this machine may do nothing other than convert

heat entirely into work, it is necessary that the machine shall return at intervals exactly to its original state; in other words, it must work in cycles. Now, just as we based the First Law on the experience of mankind, we are also relying on human experience when we declare that a perpetual motion machine of the second kind is impossible. It is, in other words, impossible to construct a machine functioning in cycles, which can convert a quantity of heat into the equivalent amount of work without producing changes elsewhere. This may be taken as one of the statements of the Second Law of Thermodynamics.

Returning to the tasks we assigned ourselves of reversing certain spontaneous processes such as the conduction of heat and the expansion of a gas into a vacuum, it will be remembered that the possibility of reversing these processes and of restoring everywhere the original state A depended on the possibility of just such a machine as the Second Law declares is impossible. For the sake of brevity and clearness we shall speak of reversible and irreversible processes but we shall use these words in a sense somewhat different from that usually employed by chemists. A process in which a system goes from state A to state B is defined to be (thermodynamically) reversible, if it is possible to restore the system to the state A without producing permanent changes of any kind anywhere else. A process is irreversible if the restoration to the original state can only be accomplished at the expense of some permanent change or changes elsewhere. Bearing these definitions in mind, we can say that the conduction of heat and the expansion of a gas into a vacuum are irreversible processes. And since a consideration of the various spontaneous processes mentioned would lead to the same result, we may state the Second Law of Thermodynamics as follows: all spontaneous processes occurring in nature are irreversible.

A consideration of the section in Chap. V on Reversible Processes and Equilibrium will show that if a system has gone from a state A to a state B by a reversible process, it is possible by reversing every infinitesimal stage to restore exactly the original conditions. Now a process can never in practice be carried out in a strictly reversible manner since that would demand that

the process be carried out infinitely slowly. We can in practice only approximate more or less closely to such a process, but that does not hinder us in the least from calculating what would be the result if we could devote an infinite time to bringing about the change. It is very much like many a problem in mechanics. Thus the laws of falling bodies deduced on the assumption that the bodies fall in a vacuum are still of great value even when the bodies actually move through the atmosphere and are retarded by friction.

We can see from the foregoing discussion that when a system goes spontaneously from state A to state B, there must be some property of the system which is essentially different in the two cases. This property is not the energy of the system since spontaneous processes can take place with a gain or loss or no change in the total energy. In the case of an isolated system (and by this we mean that we include in the system everything that is in any way concerned in the process), transformations take place without any change in the total energy of the system. It will be our next task to show that, for all processes occurring in an isolated system, a certain function of the system called the entropy always increases or in the limiting or ideal case of a reversible process remains constant. When we have shown that the entropy has such characteristics, we shall be able to say that if for any imagined process in an isolated system the total entropy will increase, then such a process can occur, but if for any imagined process we calculate that the entropy would either remain unchanged or else diminish, we can say that such a process will not take place.

Definition of Entropy

We shall define the entropy of a system by saying that for any infinitesimal stage of a strictly reversible process in which the system absorbs the infinitely small quantity of heat Q at the absolute temperature T, the increase in the entropy, S, is given by the equation

$$dS = \frac{Q}{T}, \tag{1}$$

or for a finite change in which the system goes from state 1 to state 2 by a strictly reversible process

$$S_2 - S_1 = \int_1^2 \frac{Q}{T}. \tag{2}$$

In these definitions nothing is said as to how the entropy of a system may change in irreversible processes nor does it necessarily follow from equation (2) that the difference in entropy in two states is independent of the particular reversible process employed in going from state 1 to state 2. We must prove that $S_2 - S_1$ depends only on the two states; in other words, that the entropy of a system is a function of the state of the system and does not depend on its past history. This result may also be expressed by saying that dS is a complete differential.

Carnot Cycle for any System

In Chap. V, we carried out a reversible Carnot Cycle with an ideal gas. In this process the ideal gas is restored exactly to its original state and may for the moment be left out of account. The total result of the process may be expressed by saying that a quantity of heat Q_2 has been taken isothermally from a heat reservoir at the temperature T_2, a quantity of heat Q_1 has been given to a reservoir at the lower temperature T_1 and a quantity of mechanical work W has been done. The work may be thought of as consisting in the raising of weights against gravity. We found the following relation between the quantities Q_2, Q_1, and W:

$$Q_2 = Q_1 + W. \tag{3}$$

$$W = \frac{T_2 - T_1}{T_2} Q_2. \tag{4}$$

From these equations the following is easily obtained:

$$\frac{Q_2}{T_2} = \frac{Q_1}{T_1}. \tag{5}$$

With the aid of the Second Law, viz., that it is impossible to convert a quantity of heat into the equivalent amount of work without effecting other changes, we shall prove that the nature

of the body employed in the Carnot Cycle has no effect on equations (3), (4) and (5), so long as the cycle is carried out strictly reversibly. For let us suppose that, employing any system of bodies in the reversible Carnot Cycle, and using heat reservoirs at the temperatures T_2 and T_1, we extract the same quantity of heat Q_2 at the temperature T_2, but obtain a quantity of work W' which is different from W of equation (4). We shall have from the First Law

$$Q_2 = Q_1' + W', \qquad 6)$$

if Q_1' represents the heat given to the reservoir at the temperature T_1. Let us assume, in the first instance, that W' is greater than W and hence Q_1' is less than Q_1. Carrying out a Carnot Cycle with our system, we obtain the mechanical work W' and deliver the quantity of heat Q_1' to the reservoir at T_1. Our working system is in its original state. Now let us carry out a reversed Carnot Cycle with our ideal gas. Using just a part W of the mechanical work W' that we have gained we can take the quantity of heat Q_1 (which is greater than Q_1') from the reservoir and can return the heat Q_2 to the reservoir at the higher temperature T_2. As a result of this compound cycle, everything is in its original state except that the reservoir at the temperature T_1 has lost a quantity of heat $Q_1 - Q_1'$ and we have gained an equivalent quantity of mechanical work $W' - W$. In other words, we have converted a quantity of heat into an equivalent amount of work without producing any other permanent changes. The Second Law denies the possibility of this and hence W' cannot be greater than W. But W' cannot be less than W, for in this case we could carry out the cycle with the ideal gas in the regular way and the reversed cycle with our other system and the result would be the conversion of heat into work without compensation. We must therefore conclude that the relations expressed in equations (3), (4) and (5) hold for a reversible Carnot Cycle working between the two temperatures T_1 and T_2, no matter what substance or system of substances is employed as the working medium or engine.

Change in Entropy During Carnot Cycle

From equation (1) or (2) we can easily calculate the changes in entropy during a Carnot Cycle. First, as regards the working system, we have only to consider the two isothermal processes, since during the reversible adiabatic expansion and compression, the change in entropy is zero (equation (1)). In the first isothermal stage, the working system absorbs the heat Q_2 at constant temperature T_2; its entropy increases by $\frac{Q_2}{T_2}$. In the second isothermal stage, it gives out the heat Q_1 at the temperature T_1 and its entropy diminishes by $\frac{Q_1}{T_1}$. But since $\frac{Q_2}{T_2}=\frac{Q_1}{T_1}$ (equation (5)), the entropy of the working substance does not change during a complete reversible Carnot Cycle. Now, as regards the heat reservoirs, the entropy of the one at the temperature T_2 diminishes by $\frac{Q_2}{T_2}$ and that of the other increases by $\frac{Q_1}{T_1}$ and since $\frac{Q_2}{T_2} = \frac{Q_1}{T_1}$ the total entropy of the two reservoirs does not alter. We conclude then that in a reversible Carnot Cycle carried out with any system of bodies whatever, there is no change in the total entropy of the whole system (including the working system and the reservoirs).

Any Reversible Cycle Equivalent to a Sum of Carnot Cycles

We must next show that any reversible cycle can be looked on as a combination of a number of Carnot Cycles. In Fig. 12 let *AMBSA* represent any reversible cycle carried out with any system whatever. Let the curves *AC*, *EG*, *IL*, *NP*, *RT* and *WB* represent a series of isothermals and the curves *AE*, *CD*, *FI*, *GH*, etc., represent adiabatic curves on the *p*-*V* diagram. Let us imagine the system to go through a series of changes which can be represented by the succession of points, *ACDE*, then *EGHI*, then *ILMN*, then *NPQR*, then *RTBW*, then *WSRONKIFEA*. It will be noted that the curves *ED*, *IH*, *NM* and *RQ* are traversed once in one direction and once in the opposite direction so that we can leave them out of account. Our imagined process, which it is readily seen is a combination of the simple Carnot Cycles, *ACDEA*, *FGHIF*, etc., is equivalent

to a process along the broken curves which lie close to the curves AMB and BSA. In the limit when we imagine an infinite number of isothermals to be drawn, the points $CGLPT$ will lie on the curve AMB and the points $AEIN$, etc., on the curve ASB and our combination of Carnot Cycles will be equivalent to the actual cycle. Now since in every Carnot Cycle the change in entropy is zero, the same must be true for any reversible cycle which can, as we have shown, be looked on as a combination of simple Carnot Cycles. We therefore deduce the important result that in any reversible cycle there is no change in the total entropy.

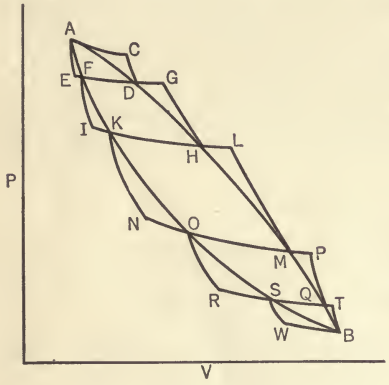


FIG. 12

The Entropy is a Function of the State of the System Only

Referring to Fig. 12, let A and B represent two states of a system. We desire to prove that the entropies of the system in the two states depend only on the two states and not on the processes, reversible or irreversible, by which the system has gone from A to B. We determine or calculate the difference in entropy $(S_B - S_A)$ by imagining the process to take place reversibly, but the actual process may have occurred in any possible way. In the first place, if the change from A to B takes place along the curve AMB and if we retrace our steps and proceed to A along the curve BMA, we have described a reversible cycle and hence the total entropy has not changed. Hence the change of entropy along a given curve is exactly reversed if we go along the curve in the opposite direction. Now the change in entropy along the curve ASB is exactly balanced by the change along the curve BMA since these two form a cycle. Hence the change of entropy along ASB is equal to the change along AMB. Hence the value of $S_B - S_A$ is independent of the particular reversible

process which we may use in calculating it. It depends on the two states only and therefore we can say that the entropy of a system in a given state depends only on the nature of that state.

Change in Entropy of an Isolated System

Let us consider an isolated system composed of any number of homogeneous bodies. We desire to determine the change in entropy which occurs when any reversible process occurs in the isolated system. Since, in a reversible process, the entropy of a body can only change if it receives or gives up heat and since the transfer of heat from one body to another is irreversible if there is a finite difference of temperature, we must suppose that all the bodies which can exchange heat are always at a common temperature. We could include in our isolated system, bodies at a higher or lower temperature than others if we supposed them to be surrounded by walls impermeable to heat. In this case however, their entropy would not change during any reversible process. Hence it involves no loss of generality if we suppose that all the homogeneous bodies are always at the common temperature T. We shall also assume that during any infinitesimal stage of the reversible process the mechanical work done by any of the bodies is given by the expression $p\,dV$. In case there should be a reversible exchange of electrical energy, the only modification in our results would be that we should have to introduce a term for the electrical work in addition to the term $p\,dV$. For the sake of simplicity we shall exclude electrical work. We shall also assume that there is no transfer of matter from one body to another, but chemical changes as long as they proceed reversibly are not excluded. Let U_1, U_2, U_3, etc., be the energies; p_1, p_2, p_3, etc., the pressures; V_1, V_2, V_3, the volumes; S_1, S_2, S_3, the entropies of bodies 1, 2, 3 . . . and T the common temperature at any instant. Let us suppose that any reversible process whatever takes place in the isolated system. For each body, we shall have equations of the following form for any infinitesimal stage of the process:

$$Q_1 = dU_1 + p_1 dV_1. \tag{7}$$

$$dS_1 = \frac{Q_1}{T} = \frac{dU_1 + p_1 dV_1}{T}. \tag{8}$$

Applied to the whole system of bodies,

$$dS_1 + dS_2 + dS_3 + \cdots = \frac{Q_1 + Q_2 + Q_3 + \cdots}{T}. \qquad (9)$$

Since the whole system is isolated, $Q_1 + Q_2 + Q_3 + \cdots = 0$ for every stage of the reversible process, hence $dS_1 + dS_2 + dS_3 + \cdots = 0$ or

$$d(S_1 + S_2 + S_3 + \cdots) = 0, \qquad (10)$$

which states therefore that in any reversible process whatever in an isolated system, there is no change in the total entropy of the system.

Change of Entropy in some Irreversible Processes

Before taking up the general problem, we shall calculate the change of entropy in one or two special cases of an irreversible process and we shall begin with the transfer of heat by conduction. In state A we have two large reservoirs at the temperatures T_1 and T_2. If these are connected by a conductor of heat, after a certain time the quantity of heat Q will have passed from one to the other, without, as we shall suppose, appreciably changing the temperature of either. This will be called state B. Now we can calculate the difference in entropy $(S_B - S_A)$ by bringing about the same changes in the two reservoirs by a reversible process. Placing any system (such as a gas) in contact with the hotter reservoir, we shall expand the system isothermally and take from the reservoir at the temperature T_2 the quantity of heat Q. We shall now expand the gas adiabatically until its temperature is T_1. Placing it in contact with the reservoir at the temperature T_1, we compress the gas isothermally and transfer to the reservoir the quantity of heat Q. What are the changes in entropy?

Reservoir at T_2. Entropy has diminished by $\frac{Q}{T_2}$.

Reservoir at T_1. Entropy has increased by $\frac{Q}{T_1}$.

The increase in entropy of the gas is easily seen to be $\frac{Q}{T_2} - \frac{Q}{T_1}$. The change in the total entropy of the reservoirs and the gas is zero, in harmony with our previous results. We are here how-

ever concerned only with the entropy of the two reservoirs which we see is greater in state B than in state A by $\frac{Q}{T_1} - \frac{Q}{T_2} = \frac{Q(T_2 - T_1)}{T_1 T_2}$ and this is positive since $T_2 > T_1$. Hence we conclude that the conduction of heat from a reservoir at a higher to one at a lower temperature is accompanied by an increase in the total entropy.

Let us also calculate the increase in entropy in another irreversible process, the expansion of a gas into a vacuum. We shall suppose that we are dealing with one mole of an ideal gas. In state A it may have the pressure p_1 and volume V_1 and in state B the pressure p_2 ($p_2 < p_1$) and volume V_2 ($V_2 > V_1$). Its temperature is the same (T) in both states. We can bring the gas by a reversible isothermal process from state A to state B in which it will absorb the quantity of heat Q from a reservoir at the temperature T. The value of Q is given by equation (25), Chap. V, and is

$$Q = RT \log_e \frac{V_2}{V_1}. \tag{11}$$

The increase in the entropy of the gas as it goes from state A to state B is therefore,

$$S_B - S_A = \frac{Q}{T} = R \log_e \frac{V_2}{V_1}, \tag{12}$$

and since V_2 is greater than V_1, this is positive and therefore in this irreversible process also there is involved an increase in the entropy.

Entropy and Irreversible Processes in General

We must emphasize once more that all irreversible processes are so because of facts which find their expression in the Second Law. If a quantity of heat could be converted into the equivalent amount of work, without causing other changes, then the so-called irreversible processes could be reversed completely. We can state the matter as follows: if any isolated system goes from a state A to a state B by an irreversible process, we can always bring state B by a reversible process into a state C which differs from the original state A solely by the fact that some reservoir

has an additional quantity of heat Q and an equivalent amount of work remains to be done. Now the entropies of the isolated system in states B and C are equal, since the system is imagined to have gone from B to C by a reversible process. We can therefore determine the change in entropy during the irreversible process in which the system went from A to B, by determining the relation between the entropies of the system in the states A and C. We shall transform the state C into a system so related to state A that we can compare the entropies in the two states. We shall suppose that in both states A and C we have a mole of an ideal gas whose volume is V_1 and whose temperature, T, is the same as that of the heat reservoir in state C which has the extra amount of heat Q. By reversible isothermal expansion of the mole of gas from volume V_1 to a larger volume V_2, we can extract the extra amount of heat Q from the reservoir and do the equivalent amount of mechanical work, and the new state, which we may call state D, has the same entropy as state C and hence the same entropy as state B. Now, the only difference between state A and state D is that in state A we have a mole of an ideal gas at a volume V_1 and a temperature T, whereas in state D the volume of the gas is V_2 and the temperature T. From equation (12) the entropy in state D is greater than in state A by $R \log_e \frac{V_2}{V_1}$, a positive quantity. Hence the entropy in state C and therefore in state B is greater than in state A. Now the change from state A to state B represented any irreversible process whatever, so that we reach the conclusion that when any irreversible process occurs in an isolated system, the total entropy increases. If an isolated system goes from state A to state B without change in entropy, then we can conclude that the process was reversible, for if it had been irreversible, then the entropy must have increased. If an isolated system goes from state A to state B and if the entropy in state B is greater than in state A, then the process must have been irreversible, for if it had been reversible, there would have been no change in the entropy. When applied to any process occurring in an isolated system, the equality or inequality of the entropy of the system in two states is not only the necessary, but

also the sufficient condition for the reversibility or irreversibility of the process. Stated mathematically, we have for any process in an isolated system

$$dS \geqq 0 \tag{13}$$

where the inequality holds for an irreversible and the equality for a reversible change. We may therefore state the Second Law of Thermodynamics in the following form: Every process occurring in nature is accompanied by an increase in the sum of the entropies of all the bodies which take part in any manner in the process. The Second Law may therefore be referred to as the Law of Increase of Entropy.

EXERCISES

1. Is it correct to say that heat cannot be converted completely into work?

2. Clausius put forward the following proposition: it is impossible to transfer heat from one body to another at a higher temperature without producing changes elsewhere. Derive this proposition from any of our statements of the Second Law.

3. Show that a machine functioning in cycles cannot produce any mechanical effect if all the processes are carried out isothermally.

4. Compare the statements: (1) in a reversible process the increase in entropy is equal to $\int_1^2 \frac{Q}{T}$; (2) in a reversible process the total entropy does not change. Is there any contradiction between these two statements? Express each of them in a way that will give no opportunity for misunderstanding.

5. What is the difference in the entropy in calories per degree of 1 gram of water at 0° C. and 1 gram of water at 100° C., the pressure being 1 atmosphere and the specific heat of water being taken as constant and equal to 1?

6. Calculate the difference in the entropy of 1 gram of ice and 1 gram of water at 0° and 1 atmosphere if the latent heat of fusion is 79.8 calories per gram.

7. Calculate the difference in the entropy of 1 mole (18.02 grams) of water at 25° C. and 1 atmosphere and 1 mole of steam at 100° C. and $\frac{1}{10}$ atmosphere. Take latent heat of evaporation at 100° C. and 1 atmosphere equal to 538.7 calories per gram and assume steam to be an ideal gas.

8. A Carnot Cycle is carried out between the temperatures T_2 and T_1. What fraction of the heat absorbed at the temperature T_2 is converted into work when the two heat reservoirs are at the temperatures (*a*) 100° C. and 20° C., (*b*) 200° C. and 30° C., (*c*) 800° C. and 30° C.?

CHAPTER VIII

DEDUCTIONS FROM THE FIRST AND SECOND LAWS

Thermodynamic Definition of Temperature

It will be remembered that in Chap. I we pointed out that a temperature scale based on one thermometric substance will in general differ from one based on any other substance. On account of the great similarity in the behavior of gases, temperatures indicated by various gases agree very accurately with each other. By a slight extrapolation it is easy to determine the behavior of a gas in the ideal state and we can consider the "absolute" temperatures which we have employed so far as being based on an ideal gas as thermometric substance. Nevertheless we shall feel better satisfied if we can define a temperature scale without the introduction of hypothetical ideal gases and we proceed to show how such a scale can be defined by the Second Law of Thermodynamics.

On the basis of the Second Law we proved in the last chapter that if we have two heat reservoirs at different temperatures and if we carry out a reversible Carnot Cycle in which we take a quantity of heat Q_2 from the warmer reservoir and deliver the quantity Q_1 to the cooler reservoir, the quantity of work W obtained in the cycle is independent of the nature of the substance which goes through the Carnot Cycle. Thus if one reservoir is at the temperature of boiling water and the other is at that of melting ice, and if the quantity of heat Q_2 is absorbed by the working substance at the higher temperature, then no matter what working substance is used, the quantity of work W obtained is always a definite fraction of Q_2, say α, so that $W = \alpha Q_2$. Now we might define a temperature scale in the following manner. Let us call the difference in temperature between melting ice and boiling water, one degree on our thermodynamic scale and let us

say that in general two bodies differ in temperature by one degree if a Carnot Cycle carried out with the two bodies as reservoirs gives us the same fraction α for the ratio of W to Q_2 as is obtained with melting ice and boiling water as the two reservoirs. In this way a scale could be constructed but it would be quite different from our ordinary one. We can, however, obtain one, which will be close to the usual one, in the following way. Since the working substance in describing a Carnot Cycle takes a larger quantity of heat from the warmer reservoir than it gives up to the colder one and since, if the temperatures of the reservoirs are maintained unchanged, the ratio of the two heat quantities is unchanged (otherwise the fraction converted into work would change) we can if we desire define the temperatures of the two reservoirs by saying that they are proportional to the two heat quantities Q_2 and Q_1 which are transferred in the Carnot Cycle. The magnitude of each degree of temperature is fixed by the additional convention that we shall call the difference in temperature of boiling water and melting ice, 100 degrees. For a Carnot Cycle working between these two temperatures, we should have, if T_0 is the temperature of the melting ice, $\frac{Q_2}{T_0 + 100} = \frac{Q_1}{T_0}$. Hence the amount of work, W, which is equal to $Q_2 - Q_1$, is given by the expression $Q_2 - \frac{T_0}{T_0 + 100} Q_2 = Q_2 \left(\frac{100}{T_0 + 100} \right)$. One accurate determination of the ratio $\frac{W}{Q_2} = \frac{100}{T_0 + 100}$ would fix the melting point of ice and the boiling point of water on this thermodynamic scale. We can easily show that the thermodynamic scale so defined is identical with that based on the laws of ideal gases. For when we employed an ideal gas in the Carnot Cycle we found that the two quantities of heat concerned were proportional to the absolute temperature on the ideal gas scale. Hence the thermodynamic scale as we have just defined it is identical with one based on the behavior of ideal gases and for most purposes may be considered as identical with that obtained using a gas such as hydrogen as the thermometric substance.

Entropy of Ideal Gases

In all cases in which the external work done in any infinitesimal stage of a reversible process is equal to $p\,dV$, we have as our definition of the change in entropy (equation (1) Chap. VII)

$$dS = \frac{Q}{T} = \frac{dU + p\,dV}{T}. \tag{1}$$

Whenever the values of U and p are known as functions of V and T, it will be possible to integrate equation (1) and obtain the expression for the change in entropy for finite changes of state. In general, we do not know the equation of state for the system under consideration and have to be content with the differential equation (1). In the case of ideal gases however we can easily integrate equation (1). For, considering one mole of the ideal gas, we have (equation (21), Chap. V)

$$dU = C_v\,dT \tag{2}$$

and also from equation (5), Chap. I,

$$pV = RT. \tag{3}$$

Substituting in equation (1), we obtain

$$dS = \frac{C_v\,dT}{T} + \frac{R\,dV}{V}. \tag{4}$$

Since C_v is assumed to be a constant for an ideal gas, we obtain on integration

$$S = C_v \log_e T + R \log_e V + \text{const.} \tag{5}$$

This may be written in the following form, if we suppose that S_1, T_1, V_1 and S_2, T_2, V_2 are the values of the entropy, temperature and volume in the initial and final states of a process:

$$S_2 - S_1 = C_v \log_e \frac{T_2}{T_1} + R \log_e \frac{V_2}{V_1}. \tag{6}$$

We can also express the entropy as a function of T and p. Thus differentiating equation (3) we obtain $p\,dV + V\,dp = R\,dT$ or $p\,dV = R\,dT - V\,dp$. Substituting this value of $p\,dV$ in the equation, $dS = \dfrac{C_v\,dT + p\,dV}{T}$ we obtain

$$dS = \frac{C_p\,dT - V\,dp}{T}, \tag{7}$$

since $C_v + R = C_p$ (equation (24), Chap. V); and since $\frac{V}{T} = \frac{R}{p}$, we have

$$dS = \frac{C_p\, dT}{T} - \frac{R\, dp}{p}. \tag{8}$$

The integral of equation (8) may be written analogously to equations (5) and (6),

$$S = C_p \log_e T - R \log_e p + \text{const.} \tag{9}$$

$$S_2 - S_1 = C_p \log_e \frac{T_2}{T_1} - R \log_e \frac{p_2}{p_1}. \tag{10}$$

It may be left as an exercise to the student to show that we have also

$$S = C_v \log_e p + C_p \log_e V + \text{const.} \tag{11}$$

$$S_2 - S_1 = C_v \log_e \frac{p_2}{p_1} + C_p \log_e \frac{V_2}{V_1}. \tag{12}$$

Entropy of a Mixture of Two Ideal Gases

Since the energy of an ideal gas depends only on its temperature, the energy of a mixture of gases is equal to the sum of the energies of each component gas when in the pure state at the same temperature. The entropy of a given mass of gas depends on two variables, say T and V or T and p, so that if we wish to determine the entropy of a mixture of two gases, whose temperature, volume and pressure are T, V and p, as a sum of the entropies of the component gases, we may be at a loss to know what values of volume and pressure are to be assigned to each gas. In other words, are we to look on the total volume of the gas as a sum of partial volumes or is the total pressure to be considered a sum of partial pressures? This question cannot be answered arbitrarily. The only way open to us is to convert the mixture of gases into two pure gases by a reversible process and calculate the change of entropy.

The vessel in Fig. 13 contains the two gases which are to be separated reversibly. The pistons AB and CD are connected rigidly to each other but are free to move in a vertical direction. The walls EF and GH are stationary. The wall EF is supposed to be permeable to gas (1) but not to gas (2); the wall CD is

permeable to gas (2) but not to gas (1). AB and GH and all other walls are impermeable to both gases. The vessel is so built that the distance AC is equal to EG and the cross section of the vessel is invariable. To simplify matters we shall suppose the vessel is placed in a vacuum. The pressure on AB is due solely to gas (1), the pressure on GH due solely to gas (2). As to the pressure on EF we shall make use of the experimental fact that if a membrane is permeable to a gas, in a state of equilibrium, that gas will exert the same pressure on both sides of the membrane, but in opposite directions. Accordingly the pressure on the piston CD will be due to gas (1) and equal to that on AB, but in the opposite direction, since the pressures on CD due to gas (2) will annul each other. Since AB and CD are rigidly connected and since the force on AB is equal and opposite to the force on CD, there is no resultant force on AB and CD considered as one system. By means of an infinitesimal force in a vertical direction on AB, the two pistons can be moved upward reversibly since we suppose that there are no frictional forces. When CD has reached EF, the two gases are completely separated and in the pure state. During this process, no finite amount of work has been done on the whole system and we shall suppose that the vessel is so enclosed that there has been no exchange of heat with the surroundings. The total energy of the system has therefore not changed. This being the case, the temperature of the gases is the same as it was originally in the mixture. Since there has been no heat exchange and since the process has been carried out reversibly, there is no change in the total entropy of this isolated system. The entropy of a mixture of two gases, whose temperature is T and volume is V is therefore the same as the sum of the entropies of each gas in the pure state at the tem-

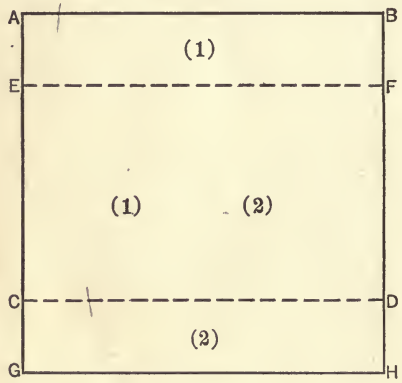


FIG. 13

perature T and same volume V as the mixture. If we wish then to express the entropy of a mixture of gases, as the sum of the entropies of each component gas, we must suppose each gas to have the same temperature and volume as the mixture, or the pressure of a gas in a mixture must be supposed to be its partial pressure as defined by equation (10) (Chap. I), since this is the pressure the gas would have when in the pure state and occupying the volume of the mixture.

Let us suppose we have a mixture of n_1 moles of gas (1) and n_2 moles of gas (2) at the temperature T and occupying a total volume V, under a total pressure p. The partial pressures p_1 and p_2 are given by the relations

$$p_1 = \frac{n_1}{n_1 + n_2} p; \qquad p_2 = \frac{n_2}{n_1 + n_2} p. \tag{11}$$

The entropy of one mole of a gas, according to equation (9), is $S = C_v \log T - R \log p + k$. The total entropy of the mixture is therefore

$$\begin{aligned} S = {} & n_1 (C_{v_1} \log T - R \log p_1 + k_1) \\ & + n_2 (C_{v_2} \log T - R \log p_2 + k_2). \end{aligned} \tag{12}$$

Evidently it is easy to prove that for a mixture of any number of ideal gases the entropy would be given by an analogous equation. We can therefore express this briefly as follows:

$$S = \sum n_1 (C_{v_1} \log T - R \log p_1 + k_1), \tag{13}$$

where p_1 is the partial pressure of gas (1). If we wish to introduce the total pressure instead of the partial pressures, we can do so in the simplest way by means of the relation, equation (11), $p_1 = \frac{n_1}{n_1 + n_2} p = x_1 p$ where x_1 is called the mole fraction of gas (1), whence we obtain, for the entropy of a mixture of gases,

$$S = \sum n_1 (C_{v_1} \log T - R \log (x_1 p) + k_1), \tag{14}$$

or

$$S = \sum n_1 (C_v \log T - R \log p + k_1) - R \sum n_1 \log x_1. \tag{15}$$

Diffusion of Gases

If we have two ideal gases originally at the same pressure p and temperature T but occupying different volumes V_1 and V_2 and if we allow them to diffuse into each other, the final state will be characterized by a total pressure p, the same temperature T and a final volume $V_1 + V_2$. The number of moles of each gas is given by the equations, $pV_1 = n_1RT$ and $pV_2 = n_2RT$. The total entropy before diffusion is

$$S_1 = n_1 (C_{p_1} \log T - R \log p + k_1) + n_2 (C_{p_2} \log T - R \log p + k_2),$$

and after diffusion is (equation (15))

$$S_2 = n_1 (C_{p_1} \log T - R \log p + k_1) + n_2 (C_{p_2} \log T - R \log p + k_2) - R (n_1 \log x_1 + n_2 \log x_2).$$

Accordingly

$$S_2 - S_1 = - R (n_1 \log x_1 + n_2 \log x_2), \tag{16}$$

and this is necessarily positive since both x_1 and x_2 are fractions.

Since $$x_1 = \frac{V_1}{V_1 + V_2} = \frac{n_1}{n_1 + n_2},$$

$$S_2 - S_1 = - R \left(n_1 \log \frac{V_1}{V_1 + V_2} + n_2 \log \frac{V_2}{V_1 + V_2} \right). \tag{17}$$

For the case in which the volumes V_1 and V_2 are equal and hence $n_1 = n_2 = n$, we shall have

$$S_2 - S_1 = 2 R n \log_e 2. \tag{18}$$

The diffusion of two gases into each other is therefore an irreversible process.

Applications to Homogeneous Bodies

Let u, s and v be the energy, entropy and volume of one gram of a homogeneous body. Each of these will be taken as functions of two variables, the temperature T and either the specific volume v or the pressure p. Since $du = \left(\frac{du}{dT}\right)_v dT + \left(\frac{du}{dv}\right)_T dv$ and since $ds = \frac{du + p\,dv}{T}$, we have $ds = \frac{1}{T}\left(\frac{du}{dT}\right)_v dT + \frac{p + \left(\frac{du}{dv}\right)_T}{T} dv.$

Also $ds = \left(\frac{ds}{dT}\right)_v dT + \left(\frac{ds}{dv}\right)_T dv$. Since the differentials dT and dv are independent, we obtain

$$\left(\frac{ds}{dT}\right)_v = \frac{1}{T}\left(\frac{du}{dT}\right)_v = \frac{c_v}{T}. \tag{19}$$

$$\left(\frac{ds}{dv}\right)_T = \frac{p + \left(\frac{du}{dv}\right)_T}{T}. \tag{20}$$

Differentiating equation (19) partially with respect to v and equation (20) with respect to T, we obtain

$$\frac{\partial^2 s}{\partial T\,\partial v} = \frac{1}{T}\left(\frac{\partial^2 u}{\partial T\,\partial v}\right) = \frac{\left(\frac{\partial^2 u}{\partial T\,\partial v}\right) + \left(\frac{dp}{dT}\right)_v}{T} - \frac{p + \left(\frac{du}{dv}\right)_T}{T^2},$$

whence

$$\left(\frac{du}{dv}\right)_T = T\left(\frac{dp}{dT}\right)_v - p, \tag{21}$$

and equation (20) becomes

$$\left(\frac{ds}{dv}\right)_T = \left(\frac{dp}{dT}\right)_v. \tag{22}$$

Employing T and p as the independent variables, we have, since

$$du = \left(\frac{du}{dT}\right)_p dT + \left(\frac{du}{dp}\right)_T dp \text{ and } dv = \left(\frac{dv}{dT}\right)_p dT + \left(\frac{dv}{dp}\right)_T dp,$$

$$ds = \frac{du + p\,dv}{T} = \left[\left(\frac{du}{dT}\right)_p + p\left(\frac{dv}{dT}\right)_p\right]\frac{dT}{T} + \left[\left(\frac{du}{dp}\right)_T + p\left(\frac{dv}{dp}\right)_T\right]\frac{dp}{T}.$$

But $ds = \left(\frac{ds}{dT}\right)_p dT + \left(\frac{ds}{dp}\right)_T dp$, and since dT and dp are independent we obtain

$$\left(\frac{ds}{dT}\right)_p = \frac{\left(\frac{du}{dT}\right)_p + p\left(\frac{dv}{dT}\right)_p}{T} = \frac{c_p}{T}. \tag{23}$$

$$\left(\frac{ds}{dp}\right)_T = \frac{\left(\frac{du}{dp}\right)_T + p\left(\frac{dv}{dp}\right)_T}{T}. \tag{24}$$

Differentiating equation (23) partially with respect to p and equation (24) with respect to T and equating the results, we obtain

$$\left(\frac{du}{dp}\right)_T = -T\left(\frac{dv}{dT}\right)_p - p\left(\frac{dv}{dp}\right)_T, \tag{25}$$

so that equation (24) becomes

$$\left(\frac{ds}{dp}\right)_T = -\left(\frac{dv}{dT}\right)_p. \tag{26}$$

Equations (19), (22), (23) and (26) are important, since they tell us how the entropy of a homogeneous body varies with the temperature, volume and pressure and express this variation in terms of quantities which are determinable by experiment. Differentiating equation (19) partially with respect to v and equation (22) with respect to T, we obtain on equating the results,

$$\left(\frac{dc_v}{dv}\right)_T = T\left(\frac{d^2p}{dT^2}\right)_v. \tag{27}$$

Similarly from equations (23) and (26) we can obtain

$$\left(\frac{dc_p}{dp}\right)_T = -T\left(\frac{d^2v}{dT^2}\right)_p. \tag{28}$$

According to equation (15), Chap. V, we have the following relation between the specific heats at constant pressure and constant volume, namely, $c_p = c_v + \left[p + \left(\frac{du}{dv}\right)_T\right]\left(\frac{dv}{dT}\right)_p$. Substituting in this the value of $\left(\frac{du}{dv}\right)_T$ from equation (21), we obtain

$$c_p = c_v + T\left(\frac{dp}{dT}\right)_v \cdot \left(\frac{dv}{dT}\right)_p. \tag{29}$$

If we make use of a relation deduced near the end of Chap. I, viz.,

$$\left(\frac{dp}{dT}\right)_v = -\frac{\left(\frac{dv}{dT}\right)_p}{\left(\frac{dv}{dp}\right)_T},$$

equation (29) becomes

$$c_p = c_v - T\left(\frac{dp}{dv}\right)_T \left(\frac{dv}{dT}\right)_p^2. \tag{30}$$

From equation (30) the difference between c_p and c_v is readily given in terms of the compressibility and coefficient of expansion and hence c_v can be calculated from c_p if the compressibility and coefficient of expansion are known. Since $\left(\frac{dp}{dv}\right)_T$ is negative, c_p is greater than c_v except when $\left(\frac{dv}{dT}\right)_p$ is zero, which happens in the case of water at 4° C. Let us calculate $c_p - c_v$ in the case of copper at 0° C. For this purpose we shall write equation (30) as follows:

$$c_p - c_v = Tv_0 \frac{\left(\frac{1}{v_0}\frac{dv}{dT}\right)_p^2}{\left(\frac{1}{v_0}\frac{dv}{dp}\right)_T} = Tv_0\frac{\alpha^2}{K}, \qquad (31)$$

where α is the cubical coefficient of expansion, K is the compressibility and v_0 is the volume of 1 gram of copper at 0° C. Using therefore the following data for copper: $v_0 = 0.112$ cc.; $T = 273$; $\alpha = 5.01 \times 10^{-5}$; $K = 8 \times 10^{-7}$, where pressures are expressed in atmospheres, we obtain on substitution

$$c_p - c_v = \frac{273 \times 0.112 \times (5.01 \times 10^{-5})^2}{8 \times 10^{-7}} = 0.0959. \qquad (32)$$

In what units is the answer expressed?

A consideration of the expression $Tv_0 \dfrac{\left(\frac{1}{v_0}\frac{dv}{dT}\right)_p^2}{\left(\frac{1}{v_0}\frac{dv}{dp}\right)_T}$ or its equivalent $-T\left(\frac{dp}{dv}\right)_T\left(\frac{dv}{dT}\right)_p^2$ will show that if p is expressed in atmospheres, v in cc., and T in the usual way, the result will be given in atmosphere-cc. per degree. To convert into calories per degree, we must multiply by 0.024205 (see Table VIII). We thus obtain for copper, $c_p - c_v = 0.0023 \dfrac{\text{cal.}}{\text{degree}}$. In the case of 63.6 grams of copper (the atomic weight) we shall have $C_p - C_v = 0.148$, and since according to the Law of Dulong and Petit the atomic heat of solid elements is approximately 6.4, we see that the

difference between the specific heats of solids at constant volume and constant pressure is very small if we can take copper as a typical example.

Applications to Actual Gases

Assuming that the behavior of an actual gas can be expressed by van der Waals' equation so long as we restrict our consideration to moderate pressures, we can obtain the following results by applying some of the equations developed in this chapter. Since $\left(\frac{dU}{dV}\right)_T = T\left(\frac{dp}{dT}\right)_v - p$ (equation (21)), on applying this to van der Waals' equation we obtain, for one mole of the gas,

$$\left(\frac{dU}{dV}\right)_T = \frac{a}{V^2}. \tag{33}$$

If the gas is heated at constant volume V and if p_0 is the pressure at 0° C., the coefficient of increase of pressure $\beta = \frac{1}{p_0}\left(\frac{dp}{dT}\right)_V$ is

$$\beta = \frac{1}{273}\left(1 + \frac{a}{p_0 V^2}\right). \tag{34}$$

If V_0 represents the volume at 0° C. and if the gas is heated at constant pressure p, the coefficient of expansion $\alpha = \frac{1}{V_0}\left(\frac{dV}{dT}\right)_p$ is

$$\alpha = \frac{1}{273}\left(1 + \frac{a}{pV^2} + \frac{a}{pV_0^2} - \frac{b}{V_0}\right). \tag{34a}$$

Similarly we obtain the following:

$$C_p = C_v + R + 2\frac{a}{VT}. \tag{35}$$

$$S = C_v \log T + R \log (V - b) + \text{const.} \tag{36}$$

Joule-Kelvin Experiment

In our discussion of the Joule-Kelvin experiment in Chap. V, we showed that if we compare the state of a given mass of gas in its initial state with that of the same mass in its final state, the value of the heat function is unchanged in the process (see equa-

tion (17), Chap. V). Referred to one mole of the gas, we have the relation

$$U_1 + p_1V_1 = U_2 + p_2V_2, \tag{37}$$

which we may express in the form,

$$d\,(U + pV) = 0. \tag{38}$$

Since $U + pV$ is a function of the two independent variables p and T, we shall have

$$d\,(U + pV) = \left(\frac{d\,(U + pV)}{dT}\right)_p dT + \left(\frac{d\,(U + pV)}{dp}\right)_T dp. \tag{39}$$

Let us suppose that there is only an infinitesimal difference of pressure dp in the Joule-Kelvin experiment and hence only an infinitesimal change in temperature dT.

Since $d\,(U + pV) = 0$, we have

$$\left(\frac{dT}{dp}\right)_{\text{J.K.}} = -\frac{\left(\frac{d\,(U + pV)}{dp}\right)_T}{\left(\frac{d\,(U + pV)}{dT}\right)_p}. \tag{40}$$

Now since $\left(\frac{d\,(U + pV)}{dp}\right)_T$ is equal to $\left(\frac{dU}{dp}\right)_T + V + p\left(\frac{dV}{dp}\right)_T$, and $\left(\frac{d\,(U + pV)}{dT}\right)_p$ is equal to C_p, making use of equation (25) we obtain

$$\left(\frac{dT}{dp}\right)_{\text{J.K.}} = \frac{T\left(\frac{dV}{dT}\right)_p - V}{C_p}. \tag{41}$$

This equation will also hold approximately for finite differences of temperature ΔT and pressures Δp, so that we have

$$\Delta T = \frac{T\left(\frac{dV}{dT}\right)_p - V}{C_p} \cdot \Delta p. \tag{42}$$

If Δp represents the decrease in pressure, then ΔT represents the fall in temperature. Assuming either the van der Waals or the Dieterici equation of state, we have approximately

$$\Delta T = \frac{\left(\frac{2a}{RT} - b\right)}{C_p} \cdot \Delta p. \tag{43}$$

This equation (43) tells us that the sign of the temperature effect depends on the relative magnitudes of $\frac{2a}{RT}$ and b. At a temperature $T = \frac{2a}{Rb}$, called the inversion temperature, there would be no temperature change; above this temperature, there would be a heating and below this temperature, a cooling effect. The Linde liquid air machine is based on the Joule-Thomson effect, since in the case of air, even at ordinary temperatures, $\frac{2a}{RT}$ is greater than b and hence there is a cooling effect. In the case of hydrogen, the value of a is extremely small, so that at ordinary temperatures and down to $-80°$ C. we have a heating effect. Below this temperature hydrogen in passing through a porous plug will have its temperature lowered.

PROBLEMS

1. Let us define the temperature (θ) on a thermodynamic scale as follows: the melting point of ice will be taken as zero and two bodies will differ by one degree when the ratio of $\frac{W}{Q_2}$ for a Carnot Cycle using these two bodies as heat reservoirs is $\frac{1}{2}$. If T is the absolute temperature on the ideal gas scale, show that $\theta = \log_2\left(\frac{T}{273}\right)$. Convert this into an expression containing the logarithm to the base 10. Calculate the values of θ corresponding to the following Centigrade temperatures, 546°, 100°, 0°, −136.5°, −200°, −272°, −272.8°, −273°.

2. Calculate the difference in the entropy of 6 grams of hydrogen originally at 0° C. and a volume of 40 liters and finally at 10° C. and a volume of 200 liters.

3. Calculate the difference in the entropy of 8 grams of oxygen originally at 15° C. and a pressure of 10 atmospheres and finally at −10° C. and a pressure of 1 atmosphere.

4. Calculate the difference in the entropy of 10 grams of air originally at a pressure of 15 atmospheres and a total volume of 1 liter and finally at a pressure of 1 atmosphere and 15 liters. Calculate also the original and final temperatures.

5. Calculate the difference between the entropy of a mixture of 2 moles of hydrogen and 1 mole of oxygen at 20° C. and a total pressure of 1 atmosphere and the sum of the entropies of the same amounts of hydrogen and oxygen in the pure state at 20° C. and 1 atmosphere.

6. What is the increase in the total entropy when 10 liters of nitrogen and 10 liters of oxygen, each at 20° C. and 1 atmosphere, diffuse into each other and form a mixture with a volume of 20 liters?

7. Deduce the relation:

$$\left(\frac{du}{dv}\right)_p = c_v\left(\frac{dT}{dv}\right)_p + T\left(\frac{dp}{dT}\right)_v - p.$$

8. Deduce the relation:

$$\left(\frac{du}{dp}\right)_v = \left(\frac{du}{dT}\right)_p\left(\frac{dT}{dp}\right)_v - T\left(\frac{dv}{dT}\right)_p - p\left(\frac{dv}{dp}\right)_T.$$

9. What are the values of $\left(\frac{du}{dv}\right)_p$ and $\left(\frac{du}{dp}\right)_v$ in the case of 1 gram of an ideal gas whose molecular weight is M?

10. Given the following data for mercury at 0° C.: $c_p = 0.0333\ \frac{\text{cal.}}{\text{degree}}$, $\frac{1}{v_0}\left(\frac{dv}{dT}\right)_p = 0.00018$ per degree; $-\frac{1}{v_0}\left(\frac{dv}{dp}\right)_T = 0.0000039$ per atmosphere; $v = \frac{1}{13.596}$ cc.; calculate the value of c_v.

11. Without making use of any deductions from the Second Law, show that

$$\left(\frac{du}{dv}\right)_p = c_p\left(\frac{dT}{dv}\right)_p - p \quad \text{and} \quad \left(\frac{du}{dp}\right)_v = c_v\left(\frac{dT}{dp}\right)_v.$$

12. By partial differentiation of $\left(\frac{du}{dv}\right)_p$ with respect to p and of $\left(\frac{du}{dp}\right)_v$ with respect to v, (using the expressions in problem 11), show that

$$(c_p - c_v)\frac{\partial^2 T}{\partial p\,\partial v} + \left(\frac{\partial c_p}{\partial p}\right)_v\left(\frac{\partial T}{\partial v}\right)_p - \left(\frac{\partial c_v}{\partial v}\right)_p\left(\frac{\partial T}{\partial p}\right)_v = 1.$$

13. From problem 12 show that for a mole of a gas for which the only assumption made is that $pV = RT$, the following expression holds:

$$C_p - C_v = R - T\left[\left(\frac{dC_p}{dT}\right)_V - \left(\frac{dC_v}{dT}\right)_p\right].$$

14. Deduce equations (34), (34a), (35), and (36) for a gas whose behavior is given by Van der Waals' equation.

15. Deduce the values of $\left(\frac{dp}{dT}\right)_V$, $\left(\frac{dp}{dV}\right)_T$ and $\left(\frac{dV}{dT}\right)$ from Van der Waals' equation and from the Dieterici equation.

16. Find the value of $\left(\frac{d(pV)}{dp}\right)_T$ using both Van der Waals' and the Dieterici equation. Find the conditions under which $\left(\frac{d(pV)}{dp}\right)_T$ is zero and interpret them. Find the value of T for which $\left(\frac{d(pV)}{dp}\right)_T$ is zero when $V = \infty$ or $p = 0$ and interpret your result.

CHAPTER IX

THERMODYNAMIC FUNCTIONS AND THERMODYNAMIC EQUILIBRIUM

In Chap. VII we learned that if any process takes place in an isolated system, the total entropy is increased or in the limiting case of a reversible process is unchanged. We can express this result symbolically as follows:

$$dS \geqq 0 \text{ (isolated system)}. \tag{1}$$

In our study of actual processes, physical or chemical or both, we shall often have to deal with systems that are not isolated. Thus if we are studying a system in which a process takes place isothermally, it is evident that in general there must be an exchange of heat or work or both with the surroundings if the temperature of the system is to remain constant. The results obtained in Chap. VII can however be applied in such a case if we bear in mind that the system plus the surroundings make up an isolated system. Since our chief concern will be with the particular system and not with the surroundings, we can without any serious loss of generality suppose that all changes in the surroundings take place reversibly. And if we let S be the entropy of the system and S_e the entropy of the surroundings, then relation (1) becomes

$$d(S + S_e) = dS + dS_e \geqq 0. \tag{2}$$

If in any infinitesimal stage of the process, Q is the heat absorbed by the system from the surroundings, W is the work done by the system on the surroundings and dU is the increase in the energy of the system, we have from the First Law

$$dU = Q - W. \tag{3}$$

Now, since we have assumed that all changes in the surroundings occur reversibly, the increase in the entropy dS_e of the surroundings is

$$dS_e = -\frac{Q}{T}. \tag{4}$$

Substituting the value of dS_e from equation (4) in relation (2), we find that the following relation holds for any infinitesimal change:

$$dS - \frac{Q}{T} \geqq 0 \quad \text{or} \quad dS - \frac{dU + W}{T} \geqq 0, \tag{5}$$

where the symbols refer to the system under consideration. As we have often pointed out, the term W includes not only mechanical work, but also electrical work, in fact any form of energy except heat. In cases in which the work is purely mechanical, W is equal to $p\,dV$ and relation (5) becomes

$$dS - \frac{dU + p\,dV}{T} \geqq 0. \tag{6}$$

In all these relations, the inequality sign holds for an irreversible and the equality sign for a reversible change of state.

Conditions of Restraint

The changes that a system may undergo are in general subject to certain conditions which we shall call conditions of restraint. Thus if we are dealing with an isothermal process, the changes of state in the system are subject to the condition that the temperature shall not change. The condition of restraint in this case can be expressed either by the equation T = constant or by the equation $\delta T = 0$. In the case of systems which do not exchange matter with the surroundings, one of the conditions of restraint is that the total mass shall not change. Suppose, however, we have a solid phase consisting of salt and a liquid phase consisting of a saturated aqueous solution in contact with the salt, and suppose we desire to deal with the solution and the solid salt as two systems. Since a transfer of salt from one phase to the other is a possible variation, the mass of each phase is no longer constant. Thus if m_1 and m_2 represent the masses of the

two phases, a condition of restraint will be that $m_1 + m_2$ is constant or $\delta m_1 + \delta m_2 = 0$. If again we have only a saturated solution of salt and no solid present and if m_1 is the mass of the solution, a possible variation will be that some salt may precipitate out, and therefore since m_1 can diminish but cannot increase, we shall have as a condition of restraint, $\delta m_1 \leqq 0$. It will be clear then that whenever a process takes place in a given system, there will always be some conditions of restraint which can usually be expressed in the form of equations, but sometimes must be given in the form of inequalities.

Isolated System

Conditions of restraint are in this case: $Q = 0$, $W = 0$ and hence $\delta U = 0$. Equations (5) and (6) become for any infinitesimal changes $dS \geqq 0$. We have already discussed this kind of system sufficiently.

Isodynamic System or Energy Constant

Condition of restraint is $\delta U = 0$. Hence $Q = W$ and equation (5) becomes $dS \geqq \frac{Q}{T}$ or $dS \geqq \frac{W}{T}$. Such a system may be represented by an ideal gas which expands isothermally so that the heat absorbed is equal to the work done.

Adiabatic System

Condition of restraint: $Q = 0$. Hence $dS \geqq 0$. If a system undergoes any adiabatic process, its entropy increases if the process is irreversible and is unchanged if the process is reversible. Such processes are sometimes called isentropic since the entropy is constant for a reversible adiabatic change of state.

Isothermal System

Condition of restraint: T = constant. Hence for any infinitesimal change of state we have

$$dS - \frac{dU + W}{T} \geqq 0. \tag{6}$$

Isothermal processes are of such great practical importance that we shall discuss them somewhat fully. Since T is constant, relation (6) is equivalent to $d(TS - U) - W \geqq 0$ or

$$d(U - TS) \leqq -W \tag{7}$$

We shall name the function $U - TS$ the free energy and denote it by the symbol F. For isothermal processes then we have

$$dF \leqq -W. \tag{8}$$

Since W is the work done by the system, $-W$ is the work done on the system; hence equation (8) means that the increase in free energy in a process is equal to or less than the work done on the system. For finite changes of state we can write

$$(F_1 - F_2)_T \geqq W. \tag{9}$$

In words, this means that in any isothermal process the decrease in the free energy of the system is equal to or greater than the work done by the system, the equality holding for reversible and the inequality for irreversible processes. We may also say that the work gained by the surroundings in an isothermal process is equal to the decrease in free energy if the process is carried out reversibly and always less than that if the process is irreversible. Hence we may say that the maximum work obtainable in an isothermal process is equal to the decrease in the free energy of the system. For processes in which the work is purely mechanical and given by $p\,dV$ for each infinitesimal stage, relations (7) and (8) become

$$d(U - TS) \leqq -p\,dV. \tag{10}$$

$$dF \leqq -p\,dV. \tag{11}$$

For reversible processes, relation (9) becomes

$$(F_1 - F_2)_T = \int_1^2 p\,dV, \tag{12}$$

whereas for irreversible processes, we shall leave relation (9) as it stands, viz.:

$$(F_1 - F_2)_T \geqq W. \tag{13}$$

When we define the free energy as given by the function $U - TS$ or when we define the loss of free energy in an isothermal process as measured by the maximum work obtainable in the process, we are adhering to the definition originally given by Helmholtz who invented the expression " free energy." It must be borne in mind however that some writers use the term "free energy" in a different sense.

Isothermal Process with Work Done Equal to Zero

If the additional constraint is imposed on the system that no work shall be done, then in addition to T = constant, we have $W = 0$. This will be the case if the volume of the system is kept constant and no other kind of work (electrical or otherwise) is obtained. Under these circumstances we shall have

$$dF \leqq 0. \tag{14}$$

or for a finite change of state at constant temperature and volume,

$$(F_1 - F_2)_{T,V} \geqq 0. \tag{15}$$

In other words, the free energy always decreases except in the case of a reversible process.

Isothermal and Isobaric Processes

The conditions of restraint are, in this case, T = constant and p = constant. It is not necessary that the pressure shall be the same in all parts of the system, but it is necessary that the pressures shall not change from their original values. We shall however consider here only the simplest case, namely where the pressure p is the same in all parts of the system. Since we are still dealing with isothermal processes, relation (7) is still valid, viz.: $d(U - TS) \leqq -W$. If we add to each side of this expression the term $p\,dV$, we shall obtain, since p is constant,

$$d(U - TS + pV) \leqq -(W - p\,dV). \tag{16}$$

The expression $U - TS + pV$ will be called the thermodynamic potential of the system and will be represented by Φ. Evidently

$$\Phi = U - TS + pV = F + pV, \tag{17}$$

so that we may express (16) as follows:

$$d\Phi \leqq -(W - p\,dV), \tag{18}$$

and therefore for a finite change of state at constant temperature and pressure,

$$(\Phi_1 - \Phi_2)_{T,p} \geqq W - p\,(V_2 - V_1). \tag{19}$$

The decrease in the thermodynamic potential in a process at constant temperature and pressure is equal to or greater than the total work done by the system minus the purely mechanical work, depending on whether the process is carried out reversibly or irreversibly. Thus if a process furnishes both electrical energy and (on account of volume changes) mechanical work, we see that the value of the electrical energy is given by $W - p\,(V_2 - V_1)$ and is therefore equal to the decrease in the thermodynamic potential $(\Phi_1 - \Phi_2)_{T,p}$ when the process is carried out reversibly.

For all cases in which the work is entirely mechanical, W is equal to $p\,dV$ or, for a finite process, equal to $p\,(V_2 - V_1)$, and equation (18) becomes

$$d\Phi \leqq 0, \tag{20}$$

and equation (19) becomes

$$\Phi_1 - \Phi_2 \geqq 0. \tag{21}$$

In other words, if a process occurs at constant temperature and pressure and if the work done is purely mechanical, then the thermodynamic potential diminishes if the process is irreversible and remains constant if the process is reversible. We may say that a system at constant temperature and pressure tends towards a minimum value of the thermodynamic potential.

Equilibrium Conditions

We can now proceed to a consideration of the conditions under which a system may be said to be in equilibrium and we shall provisionally define the meaning attached to the word equilibrium by the statement that a system is in equilibrium when its state does not change in any particular with the time. In the foregoing part of this chapter we have learned under what circumstances a process can occur in a system. The conditions are

expressed in relation (5). According to (5), an actual process can only occur if the following condition is fulfilled, viz.:

$$dS - \frac{dU + W}{T} > 0. \tag{5}$$

The equality sign holds only for reversible changes and these do not occur in nature. Hence if relation (5) cannot be fulfilled by any imagined possible process, then the system cannot change and will therefore be in equilibrium. We shall use the sign δ to indicate any imagined or virtual infinitesimal change in the state of the system, whereas the sign d will refer to any actual change. Accordingly we can assert that if a system is in equilibrium, it will remain in equilibrium, if for any virtual infinitesimal change of state consistent with the prescribed conditions of restraint,

$$\delta S - \frac{\delta U + W}{T} \leqq 0. \tag{22}$$

It is of course possible that relation (22) may be fulfilled for some virtual variations and not for others, in which case the system may be in equilibrium as regards certain variations and not as regards others. We may therefore have different degrees of stability of equilibrium and we may illustrate this fact by an example. A system consisting of a mass of water at $-5°$ C. and at atmospheric pressure is in equilibrium as regards changes in temperature and volume. A possible variation however is that an infinitesimal amount of water might change into ice at $-5°$ C. and atmospheric pressure. It may be shown that for such a virtual variation, relation (22) is not satisfied; in fact in this case we should have $\delta S - \frac{\delta U + W}{T} > 0$; and therefore as regards this virtual change, our system is not in equilibrium.

Moreover, if for any virtual variation of the state of the system, represented by a variation of the variables determining the state, the relation $\delta S - \frac{\delta U + W}{T} < 0$ is satisfied, it is usually possible to take all the variations in exactly the opposite sense, so that we shall have $\delta S - \frac{\delta U + W}{T} > 0$ and this will correspond to a

process which can occur and therefore our system will not be in equilibrium as regards this possible variation. These considerations are always true if the conditions of restraint are expressed by equations and not by inequalities. Omitting the inequality sign from (22), we have as a sufficient condition for equilibrium

$$\delta S - \frac{\delta U + W}{T} = 0, \tag{23}$$

for if this condition holds in any imagined virtual change, the change cannot as a matter of fact take place, since the necessary condition for the occurrence of any actual process is $dS - \frac{dU + W}{T} > 0$, as given in (5). Condition (23) is as we have just said a sufficient guarantee of equilibrium, but nevertheless a system may also be in equilibrium even when (23) is not satisfied. Thus if $\delta S - \frac{\delta U + W}{T}$ is negative, the system will be in equilibrium as regards certain possible variations, although not usually as regards these variations in the opposite sense. But we must recognize another important fact. Even when for a virtual variation we have $\delta S - \frac{\delta U + W}{T} > 0$, and this means that such a variation of state is actually possible, the system as a matter of fact will not always change but will often remain in equilibrium. Thus the separation of ice from undercooled water or of salt from a supersaturated solution are virtual variations for which $\delta S - \frac{\delta U + W}{T}$ will be positive and hence such processes can take place. But as a matter of fact such processes do not always occur and the system remains in equilibrium. We may say that if the laws of thermodynamics declare that a process is impossible, then the process will not occur; but if they state that a process can take place, then the process may or may not take place. The possibility of such behavior in nature gives rise to states of equilibrium which differ in stability. Thus if a system is in a state in which all conceivable virtual changes satisfy the relation $\delta S - \frac{\delta U + W}{T} = 0$, then the state is absolutely stable. If how-

ever the equation $\delta S - \frac{\delta U + W}{T} = 0$ is satisfied by some but not by all possible virtual variations, then the system is in equilibrium as regards some but not as regards all possible variations and hence the equilibrium is not absolutely stable. In these cases the equilibrium is frequently described as labile or even metastable. We shall now proceed to apply equation (23), the condition of equilibrium, to systems subjected to various restraints.

Equilibrium in Isolated System

Conditions of restraint: $Q = 0$, $W = 0$ and therefore $\delta U = 0$. Hence equation (23) becomes

$$\delta S = 0. \tag{24}$$

An isolated system is in equilibrium if all conceivable virtual variations satisfy (24) and the equilibrium will be stable. The system will also be in equilibrium as regards a certain variation, if for this variation δS is < 0. But this state will not be in general a stable state. For if we take the variation in the opposite sense, and this is usually possible, δS will be > 0 and the state of the system can change, although we cannot predict whether it will or not. As regards the relation $\delta S - \frac{\delta U + W}{T} \leqq 0$, we shall state once more that if the equality sign holds for all possible virtual variations, then the equilibrium is absolutely stable. On the other hand, if the equality sign holds for some but not for all virtual changes, or if the inequality sign holds for some variation, then the equilibrium is of a lower degree of stability. Bearing these considerations in mind, we shall content ourselves with applying the condition for stable equilibrium, $\delta S - \frac{\delta U + W}{T} = 0$.

Equilibrium in Isodynamic System

Condition of restraint: $U =$ constant or $\delta U = 0$. Hence $Q = W$ and the condition of equilibrium is

$$\delta S = \frac{W}{T} = \frac{Q}{T}. \tag{25}$$

Equilibrium in Adiabatic Process

Condition of restraint: $Q = 0$. Hence $\delta U = -W$. Therefore the condition of equilibrium is

$$\delta S = 0. \tag{26}$$

Equilibrium in Isothermal Processes

Condition of restraint: T = constant or $\delta T = 0$. The condition of equilibrium becomes

$$\delta (U - TS) + W = 0, \tag{27}$$

or if F represents the function $(U - TS)$

$$\delta F = -W. \tag{28}$$

In words, if for any virtual change of state, the increase in the free energy is equal to the work done on the system, then the system is in equilibrium. In cases in which the work is purely mechanical, equation (28) becomes

$$\delta F = -p\delta V. \tag{29}$$

Isothermal Processes and Zero Work

Conditions of restraint: T = constant and $W = 0$. The condition of equilibrium is then

$$\delta F = 0. \tag{30}$$

When the work is entirely mechanical, W becomes zero, if the volume is kept constant. Under these circumstances, $\delta V = 0$, and equation (29) reduces to equation (30). This result may be expressed as follows: A system maintained at constant volume and temperature is in equilibrium if its free energy is a minimum. That equation (30) corresponds to a minimum and not to a maximum will be clear if we consider relation (14) which tells us that in all actual isothermal processes at constant volume the free energy diminishes. We shall have equilibrium then if the free energy cannot get less, that is, if it possesses a minimum value. It must be borne in mind that these statements hold only for processes in which no work of any kind is done; in general, we must use equations (28) or (29) and not equation (30).

Isothermal and Isobaric Processes

Conditions of restraint: T = constant and p = constant. The condition of equilibrium in this case can evidently be written as follows:

$$\delta (U - TS + pV) = -(W - p\,\delta V), \tag{31}$$

or since $\Phi = U - TS + pV$ = the thermodynamic potential of the system,

$$\delta\Phi = -(W - p\,\delta V). \tag{32}$$

A system at constant pressure and temperature is in equilibrium, if for any virtual variation the decrease in the thermodynamic potential is equal to the total work done by the system minus the purely mechanical work. In the usual case in which the total work is mechanical, we have, as the condition of equilibrium,

$$\delta\Phi = 0. \tag{33}$$

If we consider relation (20) we see that in all actual variations of the state of a system the thermodynamic potential decreases. Hence we shall have a state of equilibrium if the value of Φ cannot diminish. We can therefore state the condition of equilibrium as follows: A system at constant temperature and pressure is in equilibrium if the thermodynamic potential has a minimum value.

It may be mentioned at this point that a number of writers give the name "free energy" to the function which is here called the thermodynamic potential.

Some Properties of the Characteristic Functions

We shall proceed to calculate the changes in free energy and in the thermodynamic potential for isothermal processes as functions of the temperature and either the volume or the pressure. We shall of course suppose that all changes are carried out reversibly. The process will in general be characterized by the disappearance of definite quantities of certain substances, the formation of other substances, exchange of heat with the surroundings and changes in volume and pressure. Thus a process may consist in the disappearance of two moles of hydrogen and one mole of oxygen and the formation of two moles of water. This is a

statement of the material change. In addition there will be changes in energy, depending on the temperature at which the process occurs and on the manner in which the volume or pressure varies during the given process. For the sake of brevity, we shall speak of two processes as being the same, if the same material change occurs in both. With this understanding, let us determine how the changes in free energy and the thermodynamic potential for any given material change depend on the variables T, V and p. The symbol $(F_1 - F_2)_{V,T}$ will mean the decrease in the free energy for the given process at constant temperature and constant volume; the symbols, $(F_1 - F_2)_{p,T}$, $(\Phi_1 - \Phi_2)_{p,T}$, $(\Phi_1 - \Phi_2)_{V,T}$ etc., are to be interpreted in an analogous manner. We have as our general definition of these functions for isothermal processes:

$$(F_1 - F_2)_T = U_1 - U_2 - T(S_1 - S_2). \tag{34}$$

$$\begin{aligned}(\Phi_1 - \Phi_2)_T &= U_1 - U_2 - T(S_1 - S_2) + p_1V_1 - p_2V_2 \\ &= F_1 + p_1V_1 - (F_2 + p_2V_2).\end{aligned} \tag{35}$$

Isothermal Processes at Constant Volume

From the general relation (34) we have

$$\begin{aligned}d(F_1 - F_2)_{V,T} &= dU_1 - T\,dS_1 - dU_2 + T\,dS_2 - (S_1 - S_2)\,dT \\ &= -p_1\,dV + p_2\,dV - (S_1 - S_2)\,dT.\end{aligned} \tag{36}$$

Hence we obtain the partial derivatives:

$$\left[\frac{d(F_1 - F_2)_{V,T}}{dV}\right]_T = p_2 - p_1. \tag{37}$$

$$\left[\frac{d(F_1 - F_2)_{V,T}}{dT}\right]_V = (S_2 - S_1)_V. \tag{38}$$

For the sake of clearness, let us put equations (37) and (38) into words. Equation (37) means that if a reaction is carried out, first at the temperature T and constant volume V and then at the same temperature but a larger volume $V + dV$, the decrease in free energy in the second case, $(F_1 - F_2)_{V+dV,T}$, is greater than in the first case, $(F_1 - F_2)_{V,T}$, by $(p_2 - p_1)\,dV$. Equation (38) means that a reaction is carried out in both cases at the constant volume

V, but in one case at the temperature T and in the second case at the temperature $T + dT$ and the free energy decrease in the second is greater than in the first case by $(S_2 - S_1)\,dT$. Similar interpretations can easily be given by the student to all similar equations. Substituting from (38) in equation (34) we obtain

$$(F_1 - F_2)_{V,T} = (U_1 - U_2)_{V,T} + T\left[\frac{d\,(F_1 - F_2)_{V,T}}{dT}\right]_V. \quad (39)$$

This is an extremely important equation, as it gives the relation between the free energy, total energy and temperature-coefficient of the free energy. It is one form of the Gibbs-Helmholtz equation.

Let us now consider the function $(\Phi_1 - \Phi_2)_{V,T}$. Since $(\Phi_1 - \Phi_2)_{V,T} = (F_1 - F_2)_{V,T} + (p_1 - p_2)V$, we readily obtain the following value for $d\,(\Phi_1 - \Phi_2)_{V,T}$, viz.:

$$d\,(\Phi_1 - \Phi_2)_{V,T} = V\left[\frac{d\,(p_1 - p_2)}{dV}\right]_T dV + \left[V\left(\frac{d\,(p_1 - p_2)}{dT}\right)_V + S_2 - S_1\right]dT. \quad (40)$$

Hence we have for the partial derivatives:

$$\left[\frac{d\,(\Phi_1 - \Phi_2)_{V,T}}{dV}\right]_T = V\left[\frac{d\,(p_1 - p_2)}{dV}\right]_T. \quad (41)$$

$$\left[\frac{d\,(\Phi_1 - \Phi_2)_{V,T}}{dT}\right]_V = S_2 - S_1 + V\left(\frac{d\,(p_1 - p_2)}{dT}\right)_V. \quad (42)$$

Substituting (42) in (35) we obtain

$$(\Phi_1 - \Phi_2)_{V,T} = (U_1 - U_2)_V + (p_1 - p_2)V - TV\left[\frac{d\,(p_1 - p_2)}{dT}\right]_V + T\left[\frac{d\,(\Phi_1 - \Phi_2)_{V,T}}{dT}\right]_V. \quad (43)$$

If the reacting substances are all ideal gases, and if n_1 and n_2 are the original and final number of moles, then $p_1 = \frac{n_1}{V}RT$ and $p_2 = \frac{n_2}{V}RT$. Hence $(p_1 - p_2) = \frac{(n_1 - n_2)}{V}RT$ and it is easy to show that the expression $(p_1 - p_2)V - TV\left[\frac{d\,(p_1 - p_2)}{dT}\right]_V$

vanishes. Under these circumstances, equation (43) assumes the simpler form

$$(\Phi_1 - \Phi_2)_{V,T} = (U_1 - U_2)_V + T\left[\frac{d(\Phi_1 - \Phi_2)}{dT}\right]_V. \quad (43a)$$

Isothermal Processes at Constant Pressure

We can express the decrease in free energy for an isothermal process at constant pressure in the form:

$$(F_1 - F_2)_{p,T} = (U_1 - U_2)_p - T(S_1 - S_2)_p. \quad (44)$$

On differentiation we obtain

$$\begin{aligned} d(F_1 - F_2)_{p,T} &= dU_1 - TdS_1 - dU_2 + TdS_2 - (S_1 - S_2)_p dT \\ &= -pd(V_1 - V_2) - (S_1 - S_2)_p dT \\ &= p\left[\frac{d(V_2 - V_1)}{dp}\right]_T dp \\ &\quad + \left[p\left(\frac{d(V_2 - V_1)}{dT}\right)_p + S_2 - S_1\right]dT. \end{aligned} \quad (45)$$

The partial derivatives are

$$\left[\frac{d(F_1 - F_2)_{p,T}}{dp}\right]_T = p\left[\frac{d(V_2 - V_1)}{dp}\right]_T. \quad (46)$$

$$\left[\frac{d(F_1 - F_2)_{p,T}}{dT}\right]_p = (S_2 - S_1)_p + p\left[\frac{d(V_2 - V_1)}{dT}\right]_p. \quad (47)$$

Substituting (47) in (44) we obtain

$$\begin{aligned} (F_1 - F_2)_{p,T} &= (U_1 - U_2)_p - Tp\left[\frac{d(V_2 - V_1)}{dT}\right]_p \\ &\quad + T\left[\frac{d(F_1 - F_2}{dT}\right]_p. \end{aligned} \quad (48)$$

If the reacting substances are ideal gases, it can easily be shown that (48) is equivalent to

$$(F_1 - F_2)_{p,T} = (U_1 - U_2)_p + p(V_1 - V_2) + T\left[\frac{d(F_1 - F_2)_{p,T}}{dT}\right]_p. \quad (49)$$

Or if we use the thermochemical symbol, H_p, as defined by equation (17), Chap. VI, we obtain

$$(F_1 - F_2)_{p,T} = H_p + T\left[\frac{d(F_1 - F_2)_{p,T}}{dT}\right]_p. \quad (50)$$

The function $(\Phi_1 - \Phi_2)_{p,T}$ is given by the equation

$$(\Phi_1 - \Phi_2)_{p,T} = (U_1 - U_2)_p - T(S_1 - S_2)_p + p(V_1 - V_2)_p. \quad (51)$$

On differentiation, we obtain

$$d(\Phi_1 - \Phi_2)_{p,T} = (V_1 - V_2)_p dp - (S_1 - S_2)_p dT, \quad (52)$$

since $dU_1 - T\,dS_1 = p\,dV_1$ etc. The partial derivatives are:

$$\left[\frac{d(\Phi_1 - \Phi_2)_{p,T}}{dp}\right]_T = (V_1 - V_2)_p. \quad (53)$$

$$\left[\frac{d(\Phi_1 - \Phi_2)}{dT}\right]_p = (S_2 - S_1)_p. \quad (54)$$

Substituting from (54) in (51) we obtain

$$(\Phi_1 - \Phi_2)_{p,T} = (U_1 - U_2)_p + p(V_1 - V_2)_p + T\left[\frac{d(\Phi_1 - \Phi_2)_{p,T}}{dT}\right]_p. \quad (55)$$

And since $H_p = (U + pV)_1 - (U + pV)_2$, we may write

$$(\Phi_1 - \Phi_2)_{p,T} = H_p + T\left[\frac{d(\Phi_1 - \Phi_2)_{p,T}}{dT}\right]_p. \quad (55a)$$

Equation (55a) is of especial importance since we frequently have under consideration reactions at constant temperature and constant pressure. We shall therefore find it convenient to denote the quantity $(\Phi_1 - \Phi_2)_{p,T}$ by the symbol A_p or simply A and shall call A_p the affinity of the process at constant temperature and pressure. Similarly we may call $(F_1 - F_2)_{v,T}$ the affinity of an isothermal process at constant volume and denote it by A_v. But unless otherwise specifically stated, the symbol A will be the affinity at constant pressure. Bearing these definitions in mind, we have from equations (39) and (55a)

$$A_v = H_v + T\left(\frac{dA_v}{dT}\right)_V. \quad (56)$$

$$A = A_p = H_p + T\left(\frac{dA_p}{dT}\right)_p. \quad (57)$$

The reasons for using the term affinity for the functions A_p and A_v will be given later when we discuss the conditions governing chemical equilibrium.

PROBLEMS

1. A system consisting of a supersaturated aqueous solution of sodium thiosulphate is to be maintained at constant temperature and pressure. If m_1 and m_2 are the masses of the water and the salt respectively, write down the conditions of restraint governing all possible changes in the state of the liquid phase including the possible formation of a new phase.

2. What would be the expression for the thermodynamic potential of a system consisting of an aqueous solution under a pressure p_1 and with a volume V_1, separated by a semipermeable membrane from water under a pressure p_2 and with a volume V_2?

3. Is there any difference between an isolated system and an isodynamic one?

4. Calculate the change in free energy when a mole of a liquid is evaporated at constant temperature T and constant pressure p (p = vapor pressure at temperature T), if V_1 and V_2 are the volumes of 1 mole of the liquid and of the vapor respectively. For water when $T = 373$, $p = 1$ atmosphere, $V_2 = 18.02 \times 1674$ cc. and $V_1 = 18.02$ cc. In this case give the answer in calories.

5. What is the difference in the thermodynamic potential of 1 mole of water and 1 mole of steam, both at 100° C. and 1 atmosphere?

6. Show that for any infinitesimal reversible change $d\Phi = V\,dp - S\,dT$.

7. Calculate the difference between the thermodynamical potential of a mole of water under a pressure of 2 atmospheres and a mole of water under a pressure of 1 atmosphere, the temperature being 100° C. in both cases and the water being assumed to be practically incompressible. Express the difference in calories.

8. From problems 5 and 6 how do the thermodynamic potentials of the water under 2 atmospheres and the steam under 1 atmosphere compare with each other?

9. In the case of 1 mole of an ideal gas, we have $U = C_v T + b$ (b = constant, equation (22), Chap. V) and $S = C_p \log T - R \log p + k$ (equation (9), Chap. VIII). Show that the free energy F of 1 mole of an ideal gas is $F = T(C_v - C_v \log T - R \log V + R \log R - k) + b = T(C_v - C_p \log T + R \log p - k) + b$. Show also that for 1 mole of an ideal gas $\Phi = T(C_p - C_p \log T + R \log p - k) + b$.

10. Show that for 1 mole of an ideal gas we have

$$\left(\frac{dF}{dT}\right)_V = -S;\ \left(\frac{dF}{dV}\right)_T = -p;\ \left(\frac{dF}{dT}\right)_p = -S - R;\ \left(\frac{d\Phi}{dT}\right)_p = -S;$$

$$\left(\frac{d\Phi}{dT}\right)_V = -S + R;\ \left(\frac{dF}{dp}\right)_T = V;\ \left(\frac{d\Phi}{dp}\right)_T = V;\ \left(\frac{d\Phi}{dV}\right)_T = -p.$$

11. Deduce equation (40) omitting none of the steps in the deduction.

12. State in words the meaning of equations (41), (42), (46), (47), (53) and (54).

13. What are the values of the partial derivatives (46) and (47) if the reacting substances are all gases, there being originally n_1 moles and finally n_2 moles?

14. For a certain process the value of $(\Phi_1 - \Phi_2)_{p,T}$, at 0° C. is 38,204 calories and at 10° C. 37,720 calories. Assuming that $(\Phi_1 - \Phi_2)_{p,T}$ is a linear function of the temperature, calculate the value of H_p at 0° C.

15. Deduce the relationships:

$$U = F - T\left(\frac{dF}{dT}\right)_V \quad \text{and} \quad U = \Phi - T\left(\frac{d\Phi}{dT}\right)_p - p\left(\frac{d\Phi}{dp}\right)_T.$$

CHAPTER X

FUSION, EVAPORATION AND SUBLIMATION

We shall study in this chapter systems made up of bodies in different states of aggregation, but we shall restrict our consideration to systems which have the same composition throughout. To every different, physically homogeneous part of the system we shall give the name "phase," a term introduced by Willard Gibbs. Hence on account of the restriction we have imposed, the processes of fusion, evaporation and sublimation will alter the mass but not the nature of any phase. The state of each phase will then be determined completely by its mass, and by any two of the variables, p, v and T. For the sake of clearness, we may suppose that the system is made up of one substance only, but it must be borne in mind that the results will hold for any system which conforms to the conditions we have laid down.

Since we wish to determine the conditions under which our system is in equilibrium, we may suppose it to be enclosed in a rigid vessel impermeable to heat so that all interaction with the surroundings is excluded. We have then the following conditions of restraint: the total mass, the total energy and the total volume are invariable. Let m_1, v_1, u_1, p_1, T_1, s_1 be the mass, specific volume, specific energy, pressure, temperature and specific entropy of one phase, with corresponding symbols for the other two phases, since we suppose that there are present in general three phases, solid, liquid and gaseous. If m, V and U represent the mass, volume and energy of the whole system, we have the following equations for the conditions for restraint:

$$m = m_1 + m_2 + m_3 = \text{constant}, \tag{1}$$

$$V = m_1v_1 + m_2v_2 + m_3v_3 = \text{constant}, \tag{2}$$

$$U = m_1u_1 + m_2u_2 + m_3u_3 = \text{constant}. \tag{3}$$

For the total entropy S of the system, we have

$$S = m_1 s_1 + m_2 s_2 + m_3 s_3. \tag{4}$$

The condition that this system (an isolated one) shall be in equilibrium is given by equation (24), Chap. IX and is

$$\delta S = 0. \tag{5}$$

We must therefore consider what variations our system is capable of experiencing, and we must see that they satisfy equation (5) if the system is to be in equilibrium. Evidently we can imagine a transfer of matter from one phase to another causing m_1, m_2 and m_3 to vary; the specific energies u_1, u_2 and u_3 and the specific volumes v_1, v_2 and v_3 may change and we must calculate the change in entropy due to these virtual variations. For every virtual change of energy δu and of volume δv, we have

$$\delta s = \frac{\delta u + p\,\delta v}{T}. \tag{6}$$

From equation (4) the total variation of entropy is

$$\delta S = \sum m_1\,\delta s_1 + \sum s_1\,\delta m_1, \tag{7}$$

where the summation sign applies to the three phases. Substituting from (6) we have

$$\delta S = \sum \frac{m_1\,\delta u_1}{T_1} + \sum \frac{m_1 p_1\,\delta v_1}{T_1} + \sum s_1\,\delta m_1. \tag{8}$$

We must now take into account the conditions of restraint expressed in equations (1), (2) and (3) which limit the variations. Evidently the following relations must hold:

$$\delta m_1 + \delta m_2 + \delta m_3 = 0, \tag{9}$$

$$m_1\,\delta v_1 + m_2\,\delta v_2 + m_3\,\delta v_3 + v_1\,\delta m_1 + v_2\,\delta m_2 + v_3\,\delta m_3 = 0, \tag{10}$$

$$m_1\,\delta u_1 + m_2\,\delta u_2 + m_3\,\delta u_3 + u_1\,\delta m_1 + u_2\,\delta m_2 + u_3\,\delta m_3 = 0. \tag{11}$$

In equation (8) there are nine variations, but they are not all independent since we have three equations, (9), (10), and (11), which they must satisfy. We can therefore by means of (9),

(10), and (11) reduce the number of independent variations to six; thus

$$\delta m_3 = -\delta m_1 - \delta m_2,$$

$$m_3\,\delta v_3 = -m_1\,\delta v_1 - m_2\,\delta v_2 + (v_3 - v_1)\,\delta m_1 + (v_3 - v_2)\,\delta m_2,$$

$$m_3\,\delta u_3 = -m_1\,\delta u_1 - m_2\,\delta u_2 + (u_3 - u_1)\,\delta m_1 + (u_3 - u_2)\,\delta m_2.$$

Substituting the values of δm_3, δv_3 and δu_3 in (8) we obtain

$$\begin{aligned}\delta S = &\left(\frac{m_1}{T_1} - \frac{m_1}{T_3}\right)\delta u_1 + \left(\frac{m_2}{T_2} - \frac{m_2}{T_3}\right)\delta u_2 \\ &+ \left(\frac{p_1}{T_1} - \frac{p_3}{T_3}\right) m_1\,\delta v_1 + \left(\frac{p_2}{T_2} - \frac{p_3}{T_3}\right) m_2\,\delta v_2 \\ &+ \left[s_1 - s_3 + \frac{u_3 - u_1}{T_3} + p_3\,\frac{(v_3 - v_1)}{T_3}\right]\delta m_1 \\ &+ \left[s_2 - s_3 + \frac{u_3 - u_2}{T_3} + p_3\,\frac{(v_3 - v_2)}{T_3}\right]\delta m_2.\end{aligned}$$

These six variations, δu_1, δu_2, δv_1, δv_2, δm_1 and δm_2 are independent of one another, the magnitude of any one having no relation to the magnitude of any other. If the system is to be in equilibrium and if δS is to be zero for all possible virtual variations, then the coefficients of each of the variations must be zero. Hence we obtain the following relations:

$$T_1 = T_2 = T_3 = T \text{ (equilibrium temperature)}, \tag{12}$$

$$p_1 = p_2 = p_3 = p_s \text{ (equilibrium pressure)}, \tag{13}$$

$$s_3 - s_1 = \frac{u_3 - u_1 + p_s\,(v_3 - v_1)}{T}, \tag{14}$$

$$s_3 - s_2 = \frac{u_3 - u_2 + p_s\,(v_3 - v_2)}{T}. \tag{15}$$

These six equations therefore hold for the system in equilibrium. The first four, which tell us that the temperature and pressure are uniform throughout the system, may appear rather obvious. Equations (14) and (15) are of especial interest and will be employed in the study of the phenomena of fusion, evaporation and sublimation.

Equilibrium in One Phase

Under what conditions is a system consisting of one phase only, say phase 3, in equilibrium? To answer this question we must make m_1 and m_2 equal to zero in all our equations. Let p_3 be the pressure of this single phase. A possible variation may be the formation of a second and a third phase, but in addition to the relation $\delta m_1 + \delta m_2 + \delta m_3 = 0$, we have

$$\delta m_3 \leqq 0, \quad \delta m_1 \geqq 0, \quad \delta m_2 \geqq 0.$$

As before, we find for the variation in the total entropy on putting $m_1 = 0$ and $m_2 = 0$,

$$\delta S = \left(s_1 - s_3 + \frac{u_3 - u_1 + p_3 (v_3 - v_1)}{T}\right) \delta m_1 + \left[s_2 - s_3 + \frac{u_3 - u_2 + p_3 (v_3 - v_2)}{T}\right] \delta m_2, \qquad (16)$$

where the variations δm_1 and δm_2 must be either zero or positive. Now if p_s represents the pressure at which all three phases are in equilibrium for the given value of T, we have

$$s_1 - s_3 + \frac{u_3 - u_1 + p_s (v_3 - v_1)}{T} = 0, \text{ etc.}$$

Hence, on substituting in (16), we obtain

$$\delta S = \frac{p_3 - p_s}{T} [(v_3 - v_1)\, \delta m_1 + (v_3 - v_2)\, \delta m_2]. \qquad (17)$$

Our system of one phase will be in equilibrium for the given values of p_3, v_3, T, if δS is zero or negative. Evidently, δS is zero if $p_3 = p_s$; that is, if the single phase is under a pressure at which all three phases could coexist. But we desire to see if the phase is in equilibrium when the pressure is not p_s. Since δm_1 and δm_2 are both positive, the sign of δS will depend both on $p_3 - p_s$ and on the values of $(v_3 - v_1)$ and $(v_3 - v_2)$. To simplify matters, we shall ask ourselves under what conditions will it be impossible for a single new phase, say phase 1, to appear. This simplification means that the possibility of the appearance of phase 2 is for the moment excluded, i.e. $\delta m_2 = 0$. Hence if we consider the

possibility of the formation of one new phase only, equation (17) becomes

$$\delta S = \frac{(p_3 - p_s)(v_3 - v_1)}{T} \delta m_1. \tag{18}$$

If both $(p_3 - p_s)$ and $(v_3 - v_1)$ are of the same sign, since δm_1 is positive, δS will be positive and the new phase can appear. If they are of opposite signs, δS is negative and the new phase cannot appear. To illustrate, suppose phase 3 is a gas, and phase 1 a liquid; p_s will be the vapor pressure at the temperature T. In this case v_3 is greater than v_1. Hence δS will be positive, zero or negative according as p_3 is greater than, equal to or less than p_s. In other words, a gas is in equilibrium as regards the formation of a new phase so long as its pressure is equal to or less than the pressure at which it could exist in equilibrium with the new phase. The student can easily apply (18) to other special cases. It will be seen that we have just been studying a system in which some of the conditions of restraint are given by inequalities and not by equations. Thus since the system consisted originally of phase 3 only, δm_3 could be zero or negative but could not be positive, or $\delta m_3 \leqq 0$. Similarly, $\delta m_1 \geqq 0$. It is also to be noted that even if in the present case the pressure of the gas p_3 is greater than p_s so that the formation of liquid would mean an increase in the total entropy, such a change does not always occur and the gas may remain supersaturated and in what is called labile equilibrium.

Equilibrium between Two Phases

Distinguishing the two phases by the numbers 1 and 2, we have at equilibrium,

$$T_1 = T_2 = T,$$
$$p_1 = p_2 = p_s,$$
$$s_2 - s_1 = \frac{u_2 - u_1 + p_s(v_2 - v_1)}{T}. \tag{19}$$

If we imagine one gram of phase 1 to be changed reversibly into one gram of phase 2, we have, since $ds = \frac{du + p\,dv}{T}$,

$$s_2 - s_1 = \int_1^2 \frac{du + p\,dv}{T}.$$

If we carry out the process isothermally, we have

$$s_2 - s_1 = \frac{u_2 - u_1}{T} + \frac{1}{T}\int_1^2 p\,dv. \tag{20}$$

And if we also carry out the process at constant pressure, we shall obtain equation (19). But there is another isothermal process by which we can at least conceive of one gram of phase 1 changing into one gram of phase 2 and that is by a gradual change in the volume and pressure of phase 1 without there being at any time two phases. In other words, the system is to be homogeneous throughout the change. Such a process is illustrated by the theoretical isothermal, *ABDEF* in Fig. 7 (Chap. II). Since the change in entropy $s_2 - s_1$ depends only on the initial and final states, we shall have

$$\int_1^2 p\,dv = p_s\,(v_2 - v_1), \tag{21}$$

where the value of p as a function of v is given by the equation of state of the substance. Referring again to Fig. 7, equation (21) shows that if *AF* represents p_s, the area *ABD* is equal to the area *DEF*. Hence if we know the equation of state of a substance as represented by the curve *HABDEFG*, we can determine the equilibrium pressure for the two phases at any temperature. Equations (19) for a system of two phases in equilibrium may evidently be written as follows:

$$\left.\begin{aligned} T_1 &= T_2 \\ p_1 = p_2 &= p_s \\ f_1 + p_s v_1 &= f_2 + p_s v_2 \end{aligned}\right\}, \tag{22}$$

where f is the free energy of unit mass; or in the following form, where ϕ is the thermodynamic potential of unit mass:

$$\left.\begin{aligned} T_1 &= T_2 \\ p_1 = p_2 &= p_s \\ \phi_1 &= \phi_2 \end{aligned}\right\}. \tag{23}$$

Since ϕ is defined as equal to $u - Ts + pv$,

$$\begin{aligned} d\phi &= du - T\,ds + p\,dv + v\,dp - s\,dT \\ &= v\,dp - s\,dT. \end{aligned} \tag{24}$$

Hence $$\left(\frac{d\phi}{dp}\right)_T = v \quad \text{and} \quad \left(\frac{d\phi}{dT}\right)_p = -s. \tag{25}$$

Let us suppose that our system of two phases in equilibrium suffers an infinitesimal change of state and reaches a new state of equilibrium, in which the values of the equilibrium pressure and temperature are $p_s + dp_s$ and $T + dT$. We have in general for the two phases,

$$\begin{aligned} \frac{d\phi_1}{dT} &= \left(\frac{d\phi_1}{dT}\right)_{p_1} + \left(\frac{d\phi_1}{dp_1}\right)_T \frac{dp_1}{dT} = -s_1 + v_1 \frac{dp_1}{dT}, \\ \frac{d\phi_2}{dT} &= \left(\frac{d\phi_2}{dT}\right)_{p_2} + \left(\frac{d\phi_2}{dp_2}\right)_T \frac{dp_2}{dT} = -s_2 + v_2 \frac{dp_2}{dT}. \end{aligned} \tag{26}$$

Since the new system is to be in equilibrium, we must have from equations (23)

$$\frac{d\phi_1}{dT} = \frac{d\phi_2}{dT}$$

and

$$\frac{dp_1}{dT} = \frac{dp_2}{dT} = \frac{dp_s}{dT}.$$

Hence from (26)

$$-s_1 + v_1 \frac{dp_s}{dT} = -s_2 + v_2 \frac{dp_s}{dT},$$

or taking equation (19) into consideration,

$$s_2 - s_1 = (v_2 - v_1) \frac{dp_s}{dT} = \frac{u_2 - u_1 + p_s (v_2 - v_1)}{T}. \tag{27}$$

Hence from our definition of the latent heat accompanying the transformation of one phase into another (see equation (5), Chap. VI),

$$\lambda_{12} = u_2 - u_1 + p_s (v_2 - v_1) = T (v_2 - v_1) \frac{dp_s}{dT}, \tag{28}$$

where λ_{12} is the heat absorbed when unit mass of one phase changes into unit mass of the second phase at constant temperature and pressure. Equation (28) is the famous equation discovered by Clapeyron and established by Clausius and is usually called the Clapeyron-Clausius formula. We shall proceed to illustrate the usefulness of this equation by applying it to certain examples of fusion and evaporation.

Heat of Fusion of Ice

Equation (28) may be written in the form:

$$\frac{dT}{dp_s} = \frac{(v_2 - v_1)\,T}{\lambda_f}, \tag{29}$$

where T is the temperature of fusion, λ_f the latent heat, p_s the pressure on both phases, and v_2 and v_1 the specific volumes of water and ice. We shall determine the change in the equilibrium temperature produced by changes in pressure. We can take $v_2 = 1$ cc. and $v_1 = 1.0908$ cc. and we may for our purposes suppose that v_2 and v_1 do not change appreciably for small changes in temperature and pressure. If we express pressure in atmospheres and volume in cc.'s we must express λ_f in atmosphere-cc. Now λ_f is 79.8 cal. = 3297 atmosphere-cc. Hence for a temperature near 0° C., we have, putting $T = 273$,

$$\frac{dT}{dp} = \frac{-0.0908 \times 273}{3297} = -0.0075. \tag{30}$$

For every increase in pressure of one atmosphere, the melting-point of ice is lowered 0.0075° C. In 1850 Lord Kelvin (then William Thomson) determined the melting-points of ice at pressures of 8.1 and 16.8 atmospheres and found −0.059° and −0.129°, or an average change in melting-point per atmosphere of −0.0073° and −0.0077°, in excellent agreement with equation (30). Equation (29) not only gives a qualitative but a quantitative answer to the question as to how the melting-point depends on the pressure. A qualitative answer can be given from a knowledge of the relative magnitudes of v_2 and v_1. If the liquid is denser than the solid, the substance behaves like ice, but if, as is generally the case, the solid form is denser than the liquid, the melting-point will be raised by increasing the pressure. Since ice melts at 0° C. when the pressure is one atmosphere, it will melt at +0.0075° C. in a vacuum or where the pressure is extremely small, say 4 or 5 mm.

Evaporation

The equations we have developed apply without change to the process of evaporation. We shall calculate the latent heat of evaporation of water from given values of T, $\frac{dp_s}{dT}$ and the specific volumes of liquid and vapor. We have the following data for 100° C.:

$T = 373$,

$v_2 = 1674$ cc. according to Knoblauch, Linde and Klebe,

$v_1 = 1$ cc.,

$\frac{dp_s}{dT} = 27.12 \frac{\text{mm.}}{\text{degree}} = \frac{27.12}{760} \frac{\text{atm.}}{\text{degree}}$ (Holborn and Henning),

1 atm. cc. = 0.024205 cal.

Hence the latent heat of evaporation of 1 gram of water at 100° C. is

$$\lambda = 373 \times 1673 \times \frac{27.12}{760} \times 0.024205 = 539.1 \text{ cal.},$$

in excellent agreement with values obtained by direct experiment. An approximate result can be obtained by means of a simpler formula if we assume that the vapor obeys the ideal gas laws. Under these circumstances, neglecting the specific volume of the liquid, equation (28) becomes, since $v_2 = \frac{RT}{Mp_s}$, where M is the molecular weight of the vapor,

$$\lambda = \frac{RT^2}{Mp_s} \frac{dp_s}{dT}. \tag{31}$$

Applying this to the evaporation of water at 100° C., since $R = 1.987$, $M = 18.02$, and $p_s = 1$ atmosphere,

$$\lambda = \frac{1.987 \times 373^2}{18.02} \times \frac{27.12}{760} = 547.1 \text{ cal.}$$

Our approximation formula in this case gives us a result which is between one and two per cent too high.

If we assume that λ is approximately constant over a small range of temperature, we can obtain (31) in a form which we may

call the integrated Clapeyron formula. Thus $\frac{1}{p_s}\frac{dp_s}{dT} = \frac{M\lambda}{RT^2}$, and if p_1 and p_2 are the vapor pressures at the temperatures T_1 and T_2, we obtain

$$M\lambda = 2.303\, R \frac{T_1 T_2}{T_2 - T_1} \log_{10} \frac{p_2}{p_1}, \qquad (31a)$$

where $M\lambda$ is evidently the molecular heat of evaporation, R has the value 1.987, and the factor 2.303 is introduced on account of the use of ordinary, instead of natural, logarithms.

The relation between the vapor pressure and temperature of a liquid has been expressed in a large number of empirical formulas, among which may be mentioned:

$$\log p = a + b\alpha^t + c\beta^t \text{ (Biot)},$$

$$\log p = A - \frac{B}{T} + C \log T \text{ (Kirchhoff, Rankine, Dupré)},$$

$$\log p = -\frac{L_0}{RT} + \frac{3.5}{R} \log_e T - \frac{\beta T}{R} + i \text{ (Nernst)}.$$

These formulas may be used in calculating $\frac{dp}{dT}$ from given values of p and T.

Trouton's Law

A relation, discovered independently by Pictet in 1876, by Ramsay in 1877 and by Trouton in 1884 may be stated in the form $\frac{M\lambda}{T_b} = \frac{L}{T_b}$ = constant, where L is the molar heat of vaporization at the boiling point under normal atmospheric pressure. The value of the constant is 20–21 for hydrocarbons, about 21 for esters, CO_2, H_2S and CS_2 and about 26 for water and alcohols. For substances with very low boiling points, the value of the constant is much smaller. Nernst has proposed the following formula which holds very well, not only for the substances already mentioned (excluding water and the alcohols) but also for such low boiling liquids as hydrogen, nitrogen, argon, oxygen and methane:

$$\frac{L}{T_b} = 9.5 \log_{10} T_b - 0.007\, T_b.$$

This may be referred to as the Trouton-Nernst formula.

Effect of Changes of Pressure on the Boiling Point

By a combination of the Clapeyron formula and Trouton's Rule, we can easily deduce the expression which will tell us how the boiling point of a liquid will change with slight changes in pressure. Thus, if T_b is the boiling point when the pressure is 760 mm. we have, from the modified Clapeyron equation,

$$\frac{dT_b}{dp} = \frac{T(V_2 - V_1)}{L} = \frac{RT^2}{pL}.$$

From Trouton's Rule, we have

$$\frac{L}{T_b} = k.$$

Hence
$$\frac{dT_b}{dp} = \frac{RT_b}{p} \cdot \frac{1}{k},$$

or approximately
$$\Delta T_b = \frac{R}{pk} \cdot T_b \Delta p.$$

If the pressure is expressed in millimeters, since $R = 1.987$, $p = 760$ and k is approximately 21, we obtain

$$\Delta T_b = 0.00012\ T_b \cdot \Delta p,$$

or, in general,

$$\Delta T_b = cT_b \cdot \Delta p.$$

For most ordinary substances the value of c is 0.00012; for oxygen and nitrogen it is 0.00015, and for water and the alcohols it is about 0.00010. The formula can be used to reduce observed boiling points to the normal boiling point at a pressure of 760 mm.

Effect of Pressure on Vapor Pressure of Liquid or Solid

Equations (12)–(15) and (19) are valid when the system consists of different phases of one substance in contact so that the pressure is uniform throughout the system. It is possible however, by the introduction of an indifferent gas, to have the pressure on the liquid and solid phases different from the pressure exerted by the vapor. We shall suppose for example that we have in a closed vessel, some liquid water, some water vapor and an indifferent gas at the temperature T. Let p_2 be the pressure

of the water vapor and p_1 the total pressure on the liquid. When there is no indifferent gas present, let the vapor pressure be p_s. In this case p_s is also the total pressure. Therefore, when $p_1 = p_s$, we have also $p_2 = p_s$. Let ϕ_1 and ϕ_2 be the thermodynamic potentials of 1 gram of liquid and of vapor. At equilibrium $\phi_1 = \phi_2$. According to equation (24) we have at constant temperature, $d\phi_1 = v_1\,dp_1$ and $d\phi_2 = v_2\,dp_2$ for any increase in the total pressure p_1 on the liquid and corresponding increase in pressure p_2 on the vapor. If under the new system of pressures the system is to be in equilibrium, $\phi_1 + d\phi_1$ must equal $\phi_2 + d\phi_2$ or $d\phi_1 = d\phi_2$. Hence we obtain

$$v_1\,dp_1 = v_2\,dp_2 \quad \text{or} \quad dp_2 = \frac{v_1}{v_2}\,dp_1. \tag{32}$$

Equation (32), together with the condition that when $p_1 = p_s$, $p_2 = p_s$, gives a definite solution to the problem if v_1 and v_2 are known functions of the pressure. We can obtain a fairly accurate result by assuming the liquid to be incompressible (i.e., v_1 is constant) and that the vapor obeys the gas laws. With these assumptions, we have $v_2 = \dfrac{RT}{Mp_2}$ where M is the molecular weight of the gas. Hence equation (32) becomes

$$\frac{dp_2}{p_2} = \frac{Mv_1}{RT}\,dp_1, \tag{33}$$

or integrating at constant temperature and bearing in mind that when $p_1 = p_s$, p_2 is also $= p_s$, we obtain

$$\log_{10}\frac{p_2}{p_s} = \frac{Mv_1}{2.3 \times RT}(p_1 - p_s). \tag{34}$$

Since, in general, v_2, the specific volume of saturated vapor, is very much larger than the specific volume of the liquid, it follows directly from (32) that even a very large increase in the total pressure, p_1, will produce only a small increase in the vapor pressure p_2 of the liquid. Thus at 0° C., the vapor pressure p_s of water is 4.579 mm. when the total pressure p_1 is $p_s = 4.579$ mm. Let us calculate the vapor pressure when the total pressure is 764.58 mm., i.e., when $p_1 - p_s$ is 1 atm. We have $M = 18.02$,

$v_1 = 1$ cc., $R = 82.07 \frac{\text{atm.-cc.}}{\text{degree}}$ (Table VIII, Chap. IV), $T = 273$ and $p_1 - p_s = 1$ atm. We obtain the result $\frac{p_2}{p_s} = 1.0008045$ and hence $p_2 - p_s = 0.0037$ mm. Since $p_2 - p_s$ is very small, equation (34) may usually be employed in the more convenient form

$$\frac{p_2 - p_s}{p_s} = \frac{Mv_1}{RT}(p_1 - p_s), \tag{35}$$

or equation (32) may be written as

$$\Delta p_2 = \frac{v_1}{v_2}\Delta p_1. \tag{36}$$

Thus, using equation (36), since $v_1 = 1$ cc. and $v_2 = 206{,}000$ cc., the increase Δp_2 in millimeters of mercury is related to the increase Δp_1 in atmospheres by the equation

$$\Delta p_2 = \frac{760 \times 1}{206{,}000}\Delta p_1 = 0.0037\,\Delta p_1$$

in agreement with our previous result.

The Clapeyron-Clausius formula (equation (28)) $\lambda = T(v_2 - v_1)\frac{dp_s}{dT}$ holds only when the pressure on both phases is p_s. As we have just seen, a liquid and vapor can be in equilibrium in the presence of an indifferent gas. Let the pressure on the liquid phase be p_1 and let the partial pressure of the vapor be p_2. At equilibrium we have still $T_1 = T_2$ and $\phi_1 = \phi_2$, but now $p_1 > p_2$ although the relation between p_1 and p_2 is fixed by the relation $dp_2 = \frac{v_1}{v_2}dp_1$ (equation (32)) with the additional condition that when $p_1 = p_s$, $p_2 = p_s$. We shall suppose that in any changes that may take place in the system, p_1 is kept constant, e.g., at atmospheric pressure. Equations (26) then give us

$$\frac{d\phi_1}{dT} = \frac{d\phi_2}{dT} = -s_1 = -s_2 + v_2\frac{dp_2}{dT}.$$

Hence, $s_2 - s_1 = v_2\frac{dp_2}{dT}$. Since $s_2 - s_1 = \frac{\lambda}{T}$, we have

$$\lambda = Tv_2\left(\frac{dp_2}{dT}\right)_{p_1 = \text{constant}} \tag{36a}$$

If the vapor pressure of a liquid is determined at a series of temperatures at the constant (total) pressure p_1 (e.g., one atmosphere) and if from these results we deduce the value of $\left(\frac{dp_2}{dT}\right)_{p_1 = \text{const.}}$, equation (36a) and not the Clapeyron formula gives us the latent heat of evaporation of one gram of the liquid when the pressure on the liquid is p_1. As a matter of fact, the difference between equations (28) and (36a) is negligible when the temperature of evaporation is far removed from the critical temperature, i.e., when v_1 is very small compared with v_2.

Specific Heat of Saturated Vapor

In addition to the specific heats at constant pressure and constant volume, we can define a third specific heat as the ratio of the heat absorbed to the infinitesimal elevation in temperature in the case of a phase which is maintained at a pressure at which it is in equilibrium with a second phase. When applied to the case of a vapor which is maintained at the pressure at which it is in equilibrium with its liquid phase, we shall call this specific heat the specific heat of saturated vapor. Thus if we have a gram of water vapor at a temperature T and a pressure p_s at which it would be in equilibrium with liquid water and if we raise the temperature to $T + dT$ and increase the pressure to $p_s + dp_s$ in order to maintain the vapor in the saturated condition, the ratio of heat q absorbed in this process to the elevation in temperature dT is the specific heat of saturated vapor. From the general definition of specific heat,

$$c = \frac{q}{dT} = \frac{du}{dT} + p\frac{dv}{dT}. \tag{37}$$

Since in the case of the vapor dv is negative, we see that the specific heat of saturated vapor may be positive, zero or negative. Let h_1 and h_2 be the specific heats of saturated liquid and vapor respectively. We have then,

$$h_1 = \frac{du_1}{dT} + p_s\frac{dv_1}{dT},$$

$$h_2 = \frac{du_2}{dT} + p_s\frac{dv_2}{dT}, \tag{38}$$

denoting functions relating to the liquid phase by the subscript 1 and to the vapor phase by the subscript 2. The functions u_1, u_2, p_s, v_1, v_2, etc., are determined by one variable only, for example the temperature. In general, the pressure is a function of two variables, v and T. But in the case of the two phases in equilibrium, we have the following equations:

$$\left.\begin{aligned} p_1 &= p_2 = p_s \\ T_1 &= T_2 \\ p_1 &= f_1(v_1, T_1) \\ p_2 &= f_2(v_2, T_2) \\ \int_{v_1}^{v_2} p\,dv &= p_s(v_2 - v_1). \end{aligned}\right\} \tag{38a}$$

Hence four of the six variables, p_1, p_2, v_1, v_2, T_1, T_2, can be eliminated, leaving a relation between two of the variables. Hence $\frac{dv_1}{dT}$, $\frac{dv_2}{dT}$, $\frac{dp_s}{dT}$, $\frac{du_1}{dT}$, etc., are perfectly determinate. From equations (38), we have

$$h_2 - h_1 = \frac{d(u_2 - u_1)}{dT} + p_s \frac{d(v_2 - v_1)}{dT}. \tag{39}$$

Also, since

$$\lambda = u_2 - u_1 + p_s(v_2 - v_1),$$

we obtain

$$\frac{d\lambda}{dT} = \frac{d(u_2 - u_1)}{dT} + p_s \frac{d(v_2 - v_1)}{dT} + (v_2 - v_1)\frac{dp_s}{dT}. \tag{40}$$

Accordingly, making use of the Clapeyron formula, (28)

$$h_2 - h_1 = \frac{d\lambda}{dT} - (v_2 - v_1)\frac{dp_s}{dT} = \frac{d\lambda}{dT} - \frac{\lambda}{T}. \tag{41}$$

At temperatures considerably below the critical, h_1 will be practically the same as c_{p_1}, the specific heat of the liquid at constant pressure. Therefore

$$h_2 = c_{p_1} + \frac{d\lambda}{dT} - \frac{\lambda}{T}. \tag{42}$$

In the case of saturated water vapor at 100° C., we obtain from tables, $\lambda = 538.7$, $\frac{d\lambda}{dT} = -0.61$, $c_{p_1} = 1.01$. Hence $h_2 = 1.01 - 0.61 - 1.44 = -1.04$. The specific heat of saturated water

vapor at 100° C. is negative. In other words, if a gram of water vapor at 100° C. and 760 mm. pressure has its pressure increased to the vapor pressure corresponding to 101° C. and if at the same time 1.04 calories are withdrawn, then the water vapor will be at 101° C. We may also express the results by saying that if saturated water vapor is compressed adiabatically, it becomes superheated or unsaturated; if it is adiabatically expanded, it becomes supersaturated and in general some condensation to the liquid state will take place.

The Critical State

It may happen that the values of v_1 and v_2 (calculated from equations (38a)) may become equal for some particular value of T. In such a case the two phases will become identical. Such a temperature is called a critical temperature and the pressure, volume and density corresponding to this temperature are called the critical pressure, critical volume and critical density. We shall denote these quantities by the symbols t_c, p_c, v_c, d_c. Although from the purely mathematical point of view a critical point is possible in the case of any two coexisting phases, it may not necessarily be real. We shall restrict our consideration at this point to the equilibrium between the liquid and vapor phases and determine some of the properties of the critical point. From equation (21) we have $\int_{v_1}^{v_2} p\,dv = p_s\,(v_2 - v_1)$. Let us consider the state of the system just below the critical point. Then $v_2 = v_1 + \Delta v$, where Δv is very small. Carrying out the integration by parts, we obtain

$$\int p\,dv = pv - \int v\left(\frac{dp}{dv}\right)_T dv = pv - \frac{1}{2}v^2\left(\frac{dp}{dv}\right)_T + \frac{1}{2}\int v^2\left(\frac{d^2p}{dv^2}\right)dv,$$

or inserting the limits of integration v_1 and $v_1 + \Delta v_1$,

$$\int_{v_1}^{v_1+\Delta v} p\,dv = p\,\Delta v - \frac{1}{2}[(v_1 + \Delta v)^2 - v_1^2]\left(\frac{dp}{dv}\right)_T + \frac{1}{2}\int_{v_1}^{v_1+\Delta v} v^2\left(\frac{d^2p}{dv^2}\right)dv = p_s\,\Delta v. \qquad (43)$$

Over the slight range v_1 to $v_1 + \Delta v$, the values of $\left(\frac{dp}{dv}\right)_T$ and of $\left(\frac{d^2p}{dv^2}\right)_T$ may be assumed to be constant. Since Δv is very small, equation (43) may evidently be represented as equivalent to

$$p\,\Delta v - \tfrac{1}{2}[(v_1 + \Delta v)^2 - v_1^2]\left(\frac{dp}{dv}\right)_T + \tfrac{1}{2}v_1^2\left(\frac{d^2p}{dv^2}\right)_T \Delta v = p_s\,\Delta v,$$

or dividing through by Δv, we have

$$p - \tfrac{1}{2}[2v_1 + \Delta v]\left(\frac{dp}{dv}\right)_T + \tfrac{1}{2}v_1^2\left(\frac{d^2p}{dv^2}\right)_T = p_s.$$

At the critical point, $p = p_s = p_c$. Hence

$$\left(\frac{dp}{dv}\right)_T = 0 \quad \text{and} \quad \left(\frac{d^2p}{dv^2}\right)_T = 0, \tag{44}$$

at the critical point.

Equations (44) are identical with the conditions previously found in Chap. II as obtaining at the critical point. Since $\left(\frac{dv}{dp}\right)_T$ for any substance in equilibrium is always negative, at the critical point, $\left(\frac{dv}{dp}\right)_T$ must be negative and infinitely great (equation (44)). At the critical point a substance has an infinite compressibility.

$$\left(\frac{dv}{dp}\right)_T \text{ at critical point} = -\infty. \tag{44a}$$

To simplify what is to follow, we shall assume that, for every substance, $\left(\frac{du}{dv}\right)_T$ is finite. Hence from equation (21), Chap. VIII, namely $\left(\frac{du}{dv}\right)_T = T\left(\frac{dp}{dT}\right)_v - p$, it follows that $\left(\frac{dp}{dT}\right)_v$ is always finite. We shall proceed to show that $\frac{dp_s}{dT}$ at the critical point is equal to $\left(\frac{dp}{dT}\right)_{v=v_c}$ From the Clapeyron equation, we have

$$\frac{dp_s}{dT} = \frac{\lambda}{T(v_2 - v_1)} = \left(\frac{s_2 - s_1}{v_2 - v_1}\right)_T. \tag{45}$$

For a state infinitely close to the critical point, equation (45) evidently becomes

$$\frac{dp_s}{dT}\text{ (at critical point)} = \left(\frac{ds}{dv}\right)_{T=T_c},$$

and from equation (22), Chap. VIII, we obtain

$$\frac{dp_s}{dT}\text{ (at critical point)} = \left(\frac{dp}{dT}\right)_{v_c}. \qquad (46)$$

The proof of this theorem can be established in various ways, but that just given is probably the simplest. Since $\left(\frac{dp}{dT}\right)_v$ is always finite (see above), $\frac{dp_s}{dT}$ at the critical point is a finite quantity. From the perfectly general equation, $\left(\frac{dv}{dT}\right)_p = -\left(\frac{dv}{dp}\right)_T\left(\frac{dp}{dT}\right)_v$, (where p, v, and T are connected by one relation), we have, since $\left(\frac{dv}{dp}\right)_T$ is negative and infinitely great at the critical point and since $\left(\frac{dp}{dT}\right)_v$ is always finite,

$$\text{(at critical point)}\left(\frac{dv}{dT}\right)_p = +\infty, \qquad (47)$$

or the coefficient of expansion at the critical point is positive and infinitely great.

If we represent p_s as a function of v_1 and v_2, on a diagram in which the ordinates represent pressures and the abscissæ volumes, we shall find, starting with the liquid phase, that as v_1 is increased p_s increases until v_1 equals v_c, the critical volume, when a maximum value of p_s is reached. Larger values of v correspond to v_2, the volume of the vapor phase, and as v_2 increases the corresponding value of p_s diminishes. In general, then, $\frac{dp_s}{dv_1}$ is positive and $\frac{dp_s}{dv_2}$ is negative, but at the critical point each becomes zero. Since

$$\frac{dT}{dv_1} = \left(\frac{dT}{dv_1}\right)_p + \left(\frac{dT}{dp}\right)_{v_1}\frac{dp_s}{dv_1},$$

and

$$\frac{dT}{dv_2} = \left(\frac{dT}{dv_2}\right)_p + \left(\frac{dT}{dp}\right)_{v_2}\frac{dp_s}{dv_2},$$

it is clear that at the critical point $\frac{dT}{dv_1} = 0$ and $\frac{dT}{dv_2} = 0$. It is easy to show that at the critical point

$$\frac{dv_1}{dT} = +\infty \quad \text{and} \quad \frac{dv_2}{dT} = -\infty, \tag{48}$$

by realizing that near the critical point $\frac{dv_1}{dT}$ is always positive and $\frac{dv_2}{dT}$ is always negative.

Latent Heat

Since $\lambda = T(v_2 - v_1)\frac{dp_s}{dT}$, at the critical point $\lambda = 0$, since $v_2 = v_1$ and $\frac{dp_s}{dT}$ and T are finite. Since λ is also equal to $u_2 - u_1 + p_s(v_2 - v_1)$, we have

$$\frac{d\lambda}{dT} = \frac{du_2}{dT} - \frac{du_1}{dT} + p_s\left(\frac{dv_2}{dT} - \frac{dv_1}{dT}\right) + (v_2 - v_1)\frac{dp_s}{dT},$$

or

$$\frac{d\lambda}{dT} = \frac{du_2}{dT} - \frac{du_1}{dT} + p_s\left(\frac{dv_2}{dT} - \frac{dv_1}{dT}\right) + \frac{\lambda}{T}. \tag{49}$$

Also

$$\frac{du_1}{dT} = \left(\frac{du_1}{dT}\right)_v + \left(\frac{du_1}{dv_1}\right)_T \frac{dv_1}{dT} = c_{v_1} + \left(\frac{du_1}{dv_1}\right)_T \frac{dv_1}{dT};$$

hence

$$\frac{d\lambda}{dT} = c_{v_2} - c_{v_1} + \left[p_s + \left(\frac{du}{dv}\right)_T\right]\left(\frac{dv_2}{dT} - \frac{dv_1}{dT}\right) \tag{50}$$

at the critical point, since $\lambda = 0$, and $\left(\frac{du_1}{dv_1}\right)_T = \left(\frac{du_2}{dv_2}\right)_T$, since the phases are identical. But we have shown that at the critical point $\frac{dv_2}{dT}$ is $-\infty$ and $\frac{dv_1}{dT}$ is $+\infty$; hence at the critical point

$$\frac{d\lambda}{dT} = -\infty. \tag{51}$$

We assume that the specific heat at constant volume is always positive and finite. Since, however, we have (equation (29), Chap. VIII) $c_p = c_v + T\left(\frac{dp}{dT}\right)_v\left(\frac{dv}{dT}\right)_p$, it follows that at the crit-

ical point, the specific heat at constant pressure is positive and infinitely great, since $\left(\frac{dv}{dT}\right)_p = \infty$.

We summarize in the following list some of the important relations which we have found to hold for the critical point.

$$\left(\frac{dp}{dv}\right)_T = 0 \quad \text{or} \quad \left(\frac{dv}{dp}\right)_T = -\infty. \tag{44}$$

$$\frac{dp_s}{dv_1} = 0 \quad \text{or} \quad \frac{dv_1}{dp_s} = +\infty.$$

$$\frac{dp_s}{dv_2} = 0 \quad \text{or} \quad \frac{dv_2}{dp_s} = -\infty,$$

$$\left(\frac{d^2p}{dv^2}\right)_T = 0. \tag{44}$$

$$\left(\frac{dp}{dT}\right)_{v_c} = \frac{dp_s}{dT} = \text{finite}. \tag{46}$$

$$\left(\frac{dT}{dv}\right)_p = 0 \quad \text{or} \quad \left(\frac{dv}{dT}\right)_p = +\infty. \tag{47}$$

$$\frac{dT}{dv_1} = 0 \quad \text{or} \quad \frac{dv_1}{dT} = +\infty. \tag{48}$$

$$\frac{dT}{dv_2} = 0 \quad \text{or} \quad \frac{dv_2}{dT} = -\infty. \tag{48}$$

$$\lambda = 0.$$

$$\frac{d\lambda}{dT} = -\infty. \tag{51}$$

$$c_p = +\infty.$$

The Law of Cailletet and Mathias

Cailletet and Mathias in 1886 discovered a remarkable and very useful relationship between the densities of saturated liquid and vapor. According to them, the mean of the orthobaric densities of liquid and vapor is a linear function of the temperature. Thus,

if d_1 and d_2 (the reciprocals of v_1 and v_2) are the orthobaric densities of liquid and vapor, we have

$$\frac{d_1 + d_2}{2} = d_0 + \alpha t, \tag{52}$$

where d_0 is the mean density at 0° C. and α is a constant and negative. This law is frequently referred to as the law of the rectilinear diameter. It holds with a considerable degree of accuracy for many substances and provides one of the best methods of determining the critical density, d_c, for evidently we have

$$d_c = d_0 + \alpha t_c. \tag{53}$$

In cases in which equation (52) is not sufficiently accurate over a wide range of temperatures, the critical density can be obtained by determining the values of $\frac{d_1 + d_2}{2}$ at temperatures in the neighborhood of the critical temperature and then, by a slight extrapolation, the value of d_c.

PROBLEMS

1. Calculate the latent heat of sublimation of ice at −20° C. from the following vapor pressure data:

0.808 mm. at −19.5°; 0.770 mm. at −20°; 0.734 mm. at −20.5°.

2. Calculate the latent heat of evaporation of water at 0° C. and at 27° C. from the vapor pressure data:

+0.5° C. . . . . 4.750 mm.	27.1° C. . . . . 26.905 mm.
0.0° C. . . . . 4.579 mm.	27.0° C. . . . . 26.747 mm.
−0.5° C. . . . . 4.414 mm.	26.9° C. . . . . 26.590 mm.

3. In the case of ammonia, we have the following vapor pressure data:

t	p	v_1	v_2
	Atm.	cc.	cc.
20° C.	8.41	1.634	148.0
15° C.	7.14	1.616	174.1
10° C.	6.02	1.598	206.0
5° C.	5.04	1.582	245.2
0° C.	4.19	1.566	293.9

Calculate the latent heat of evaporation of ammonia at 5°, 10° and 15° C., (*a*) assuming ammonia vapor to be an ideal gas; (*b*) using the values of v_1 and v_2 given in the table.

4. Using the integrated Clapeyron formula (31a), calculate λ for water near 0° C. from the vapor pressures at 0.5° C. and −0.5° C.

5. Employ the integrated Clapeyron formula in calculating the latent heat of evaporation of ammonia near 10° C.

6. The latent heat of fusion of acetic acid at its normal melting-point, 16.6° C., is 46.4 calories. The density of the solid is 1.2658 and that of the liquid is 1.0532. At what temperature will acetic acid melt when the pressure is 10 atmospheres?

7. Calculate the vapor pressure of water at 100° C. and under a pressure of two atmospheres.

8. The orthobaric vapor pressure of ether at 0° C. is 184.9 mm. What will be the vapor pressure if the pressure on the liquid ether is increased by 10 atmospheres, given $v_1 = 1.358$ cc., and $v_2 = 1209$ cc.?

9. At what angle do the vapor pressure curves for ice and water meet, the pressures being plotted in millimeters of mercury?

10. If the subscripts 1 and 2 denote liquid and vapor phases which are always maintained in equilibrium, show that, at the critical point,

$$\frac{du_1}{dv_1} = \frac{du_2}{dv_2} = \left(\frac{du}{dv}\right)_T.$$

11. In the case of normal pentane, at 0° C., $d_1 = 0.6454$ and $d_2 = 0.0008$; at 190° C., $d_1 = 0.3445$ and $d_2 = 0.1269$. Calculate the value of α in the equation of Cailletet and Mathias. If 197.2° C. is the critical temperature, calculate the critical density of normal pentane. Young gives 0.2323 as the value of d_c.

CHAPTER XI

THE PHASE RULE

In the last chapter we discussed the conditions of equilibrium in a system subject to the restriction that the composition of all the phases was to be the same and was to be invariable. We shall now proceed to a consideration of systems to which this restriction is no longer applied. We have already defined the phases of a system as consisting of every different, physically homogeneous part of the system. We turn our attention now to the problem of fixing the composition of the phases.

In the case of a phase of invariable composition (such as water vapor), the external variables, U, S, V, Φ are determined by the mass of the phase and any two of the internal variables, p, v, T, etc. The internal variables, u, s, v, ϕ, etc., are independent of the mass of the phase but are determined by any two internal variables. If, however, a system contains phases which can change their composition when there is an exchange of matter between two or more phases, then the external variables, (e.g., U, the total energy) will depend not only on two internal variables (e.g., p and T) but also on the masses of several substances. The number of these substances, radicals or elements, whose masses determine, together with p and T, the values of the external variables for every phase of the system, is said to be the number of independent components or simply the components of the system. The internal variables in any phase are from their nature independent of the total mass of the phase and are therefore determined by p, T and the ratios of the masses of the independent components; for doubling the total mass of the phase and therefore doubling the mass of every component in the phase at constant temperature and pressure will not affect the specific volume v of the phase or the value of any other internal variable.

Suppose we dissolve 10 grams of sodium chloride in 100 grams

of water. The total volume V depends on p, T and the masses of water and of salt. The specific volume v or its reciprocal, the density, depends on p, T and the ratio of the mass of water to the mass of salt. Such a system has therefore two components. It must be borne in mind that it is a matter of indifference to us what chemical changes may take place in the phase. From the standpoint of the atomic and molecular theories and the theory of ionization, it is probable that in the salt solution we have a number of different molecular species present, e.g., H_2O, $(H_2O)_2$, $(H_2O)_3$, NaCl, $\overset{+}{Na}$, $\overset{-}{Cl}$ and others. It is possible that the ions are hydrated and other chemical changes are conceivable. From our point of view however the state of the solution (whatever it may be in detail) is determined completely by p, T and the masses of water and salt used in making the solution or obtainable from it.

Let us consider another and more complicated case. Suppose that on analyzing an aqueous solution, a chemist reported that it contained W grams of water, a equivalents of sodium, b equivalents of potassium, c equivalents of the nitrate radical and d equivalents of the chloride radical. In the solution, in addition to water, there might have been present, to use the molecular symbols, NaCl, KNO_3, $NaNO_3$, KCl, $\overset{+}{Na}$, $\overset{+}{K}$, $\overset{-}{Cl}$, $\overset{-}{NO_3}$. Let us see how many independent components there are. The report of the analyst might lead one to think that there were five independent components, viz.: water, and the four radicals, Na, K, Cl and NO_3, or water and the four salts NaCl, KNO_3, $NaNO_3$, KCl. But from the character of the substances in solution, we have the restriction that $a + b$ must equal $c + d$, or $d = a + b - c$. The analyst might have omitted the number of equivalents of the chloride radical, since that is determined by a, b, c. Hence we see that the solution in question, which may be described if we desire as an aqueous solution of NaCl, KNO_3, $NaNO_3$, and KCl, is a system of four independent components. The student can easily convince himself that the given solution can be reproduced by taking W grams of water and suitable amounts of any three of the four salts.

We may add one more illustration. If we form a gaseous phase by taking a moles of PCl_3 and b moles of Cl_2 and maintain the temperature at 250° C. and the pressure at one atmosphere, the total volume of the phase will depend on a and b, i.e., on two masses. Now this phase is believed to contain three substances, PCl_3, Cl_2 and PCl_5, the last because we have a (chemically) reversible action represented by the equation $PCl_3 + Cl_2 \rightleftarrows PCl_5$, but evidently the state of the system is determined by our statement of the amounts of PCl_3 and of Cl_2 used in forming it. Exactly the same system would be obtained if we were to start with a moles of PCl_5 and $(b-a)$ moles of Cl_2. Hence we have in this case a system of two components. The system is completely defined by giving the temperature, the pressure and the masses of PCl_3 and Cl_2 to be used in reproducing the system. This means, for example, that when p, T, a, and b are fixed the actual masses of PCl_3, of Cl_2 and PCl_5 in the equilibrium mixture are thereby determined. It does not mean that they are known but that they are absolutely fixed. Whether or not we can actually find out the masses of the various substances present depends sometimes on our experimental skill and sometimes on hypotheses as to the nature of the system. Thus if we assume that PCl_3, Cl_2 and PCl_5 behave as ideal gases in the mixture, then a knowledge of the density of the equilibrium mixture, in addition to a knowledge of T, p, a and b, will enable us to calculate the actual amounts of the three substances.

Degrees of Freedom

We shall define the number of degrees of freedom of a system as equal to the number of internal variables which may be altered arbitrarily (within certain limits) without causing the disappearance of any phase or the formation of a new phase. Thus a system consisting of liquid water only may have its temperature and pressure altered independently and arbitrarily within wide limits without causing the formation of any new phase. It is therefore a system of two degrees of freedom or a divariant system. If we have liquid water and water vapor coexisting, we may alter the temperature arbitrarily, but if we are to have the two phases

still in equilibrium the pressure must be changed in a way that is determined by the alteration in temperature. This is therefore a univariant system or one with one degree of freedom.

System of N Components in P Phases

We shall distinguish the different phases by accents and the different components by numeral subscripts. Thus Φ' is the total thermodynamic potential of phase 1 and m_1' is the mass of component 1 in phase 1. We shall suppose that no phases are separated by walls or membranes so that the pressure p is uniform throughout the system. Evidently the temperature T must also be the same throughout the system when in equilibrium. We shall also assume for the present that each component is found in every phase. In order to determine the conditions of equilibrium, we shall consider infinitesimal virtual variations of the variables of the system and calculate the variation $\delta\Phi$ of the thermodynamic potential of the whole system. We have first of all

$$\Phi = \Phi' + \Phi'' + \ldots \Phi^p. \tag{1}$$

If m_1 is the total mass of component 1, we have

$$\left.\begin{aligned} m_1 &= m_1' + m_1'' + \ldots m_1^p \\ m_2 &= m_2' + m_2'' + \ldots m_2^p \\ &\vdots \\ m_n &= m_n' + m_n'' + \ldots m_n^p. \end{aligned}\right\} \tag{2}$$

The thermodynamic potential Φ' of phase 1, like any other external variable, is a function of T, p and $m_1', m_2', \ldots m_n'$ or

$$\Phi' = f(T, p, m_1', m_2', \ldots m_n'). \tag{3}$$

Hence we may write

$$d\Phi' = \left(\frac{d\Phi'}{dT}\right)_{p, m_1' \ldots m_n'} dT + \left(\frac{d\Phi'}{dp}\right)_{T, m_1' \ldots m_n'} dp + \sum_1^n \left(\frac{d\Phi'}{dm_1'}\right)_{T, p, m_2' \ldots m_n'} dm_1'. \tag{4}$$

For a phase of invariable composition (dm_1', etc. = 0), we have $d\Phi = -S\,dT + V\,dp$. Let us also define the function μ by the equation

$$\mu_1' = \left(\frac{d\Phi'}{dm_1'}\right)_{T, p, m_2' \ldots mn'}. \tag{5}$$

Then equation (4) becomes

$$d\Phi' = -S'dT + V'dp + \mu_1'dm_1' + \ldots \mu_n'dm_n' \ldots \quad (6)$$

T and p are unaccented because they have the same values in all phases. We shall now show that the functions μ_1', μ_2', etc., are internal variables, i.e., that they are independent of the total mass of the phase but determined by the specific properties of the phase. Suppose that all the components in phase 1 have their masses increased n times, the temperature and pressure being unchanged. Then the total volume, the total energy, the total entropy and the total thermodynamic potential will be increased n times. Now if we are to bring about the same change of state in our larger phase as is represented by equation (6) for the smaller phase, every term in equation (6) must be increased n-fold. For example, dm_1', etc., will be n times as large, V' will be n times as large, and $d\Phi'$ will be n times as large. Hence μ_1', μ_2', etc., are unchanged. Therefore we conclude from equation (5) that each μ is a function of T, p and the $N - 1$ ratios of the N components and is therefore determined entirely by what we have called internal variables. The virtual variation in Φ will from equation (1) be given by

$$\delta\Phi = \delta\Phi' + \delta\Phi'' + \ldots \delta\Phi^p. \quad (7)$$

Since at equilibrium T and p must have the same values in all the phases, the variations δT and δp must be the same for all phases. Hence substituting equation (6) and similar equations for the other phases in equation (7), we obtain

$$\begin{aligned}\delta\Phi = (-S' - S'' \ldots -S^p)\,\delta T + (V' + V'' + \ldots V^p)\,\delta p \\ + \mu_1'\,\delta m_1' + \mu_1''\,\delta m_1'' + \cdots + \mu_1^p\,\delta m_1^p \\ + \mu_2'\,\delta m_2' + \mu_2''\,\delta m_2'' + \cdots + \mu_2^p\,\delta m_2^p \\ \vdots \qquad\qquad \vdots \qquad\qquad \vdots \\ + \mu_n'\,\delta m_n' + \mu_n''\,\delta m_n'' + \cdots + \mu_n^p\,\delta m_n^p\end{aligned} \quad (8)$$

From equation (8) we can deduce the conditions of equilibrium and we shall do so for a system in which the temperature and pressure are to be maintained constant. In this case, according

to equation (33), Chap. IX, the condition of equilibrium is that $\delta\Phi$ shall vanish. Since δT and δp are to be zero, the condition that $\delta\Phi$ shall be equal to zero means that the expression on the right hand side of equation (8) shall equal zero.

Now, eliminating the terms containing δT and δp, we see that the remaining terms have to do with the transfer of the various components from one phase to another. If the system is in equilibrium there will be no interchange of matter between the phases and the condition that there shall be no interchange is that the sum of all the terms on the right hand side shall equal zero. Now the variations $\delta m_1'$, $\delta m_1''$, etc., are not independent, for the sum of the masses of each component in all the phases is a constant or from the set of equation (2) we have

$$\left.\begin{array}{l} \delta m_1 = 0 = \delta m_1' + \delta m_1'' + \ldots \delta m_1^{p} \\ \delta m_2 = 0 = \delta m_2' + \delta m_2'' + \ldots \delta m_2^{p} \\ \vdots \qquad\quad \vdots \qquad\quad \vdots \qquad\quad \vdots \\ \delta m_n = 0 = \delta m_n' + \delta m_n'' + \ldots \delta m_n^{p} \end{array}\right\} \tag{9}$$

Hence $\delta\Phi$ can be zero for all possible variations, only if, in addition to $\delta T = 0$ and $\delta p = 0$, we have

$$\left.\begin{array}{l} \mu_1' = \mu_1'' = \mu_1''' = \ldots \mu_1^{p} \\ \mu_2' = \mu_2'' = \mu_2''' = \ldots \mu_2^{p} \\ \vdots \qquad \vdots \qquad \vdots \qquad\quad \vdots \\ \mu_n' = \mu_n'' = \mu_n''' = \ldots \mu_n^{p} \end{array}\right\} \tag{10}$$

Calling μ_1' the chemical potential of component 1 in phase 1, we see that when a system is in equilibrium, the chemical potential of any component is the same in all the phases. We can now calculate the number of degrees of freedom of our system. The total number of internal variables includes p and T and the ratios of the masses of the N components in P phases; in all $2 + P(N-1)$. The number of conditions or equations which have to be satisfied by the system in equilibrium is given by the set of equations (10) and these amount to $N(P-1)$. The number of internal variables which are left indeterminate and which therefore may be altered arbitrarily is $2 + P(N-1) - N(P-1)$

$= N + 2 - P$. Hence the number of degrees of freedom F of a system of N independent components in P phases is

$$F = N + 2 - P. \qquad (11)$$

This is the famous phase rule, first enunciated by Willard Gibbs * (1875–1878).

It will be remembered that we assumed that each of the N components was found in every one of the P phases. If however a certain component is absent from a given phase, the number of ratios of masses of components in that phase will be one less than we have supposed and therefore the total number of internal variables will be diminished by one. But at the same time the chemical potential for that component in the given phase will be absent from the set of equations (10) and accordingly the number of conditions to be satisfied will be diminished by one. Hence equation (11) will still be valid.

Chemical Potentials

The chemical potentials of the various components of a system may be defined with reference to functions other than Φ. Thus restricting our consideration to a single phase and omitting the accents, we may write equation (6) in the following forms (since $d\Phi = dU - T\,dS + p\,dV - S\,dT + V\,dp$):

$$dU = T\,dS - p\,dV + \mu_1\,dm_1 + \mu_2\,dm_2 + \cdots + \mu_n\,dm_n \quad (12)$$

$$d(U+pV) = T\,dS + V\,dp + \mu_1\,dm_1 + \mu_2\,dm_2 + \cdots \mu_n\,dm_n \quad (13)$$

$$dF = d(U - TS) = -S\,dT + p\,dV + \mu_1\,dm_1 + \cdots + \mu_n\,dm_n \quad (14)$$

From equations (6), (12), (13) and (14), it is evident that the chemical potential of component 1 in the phase may be defined by any of the following equations:

$$\mu_1 = \left(\frac{d\Phi}{dm_1}\right)_{T,\,p,\,m_2 \ldots m_n} = \left(\frac{dU}{dm_1}\right)_{S,\,V,\,m_2 \ldots m_n} = \left(\frac{dF}{dm_1}\right)_{T,\,V,\,m_2 \ldots m_n}$$
$$= \left[\frac{d(U+pV)}{dm_1}\right]_{S,\,p,\,m_2 \ldots m_n}.$$

* See the Scientific Papers of J. Willard Gibbs, Vol. I, p. 96.

We can interpret equation (6) in the following manner. Omitting accents, we can suppose that $d\Phi$ is the thermodynamic potential of an infinitely small portion of a phase and that this infinitesimal portion of the phase contains the masses dm_1, dm_2, etc., of the N components. Since the phase is homogeneous, $dm_1 : dm_2 : \ldots dm_n = m_1 : m_2 : \ldots m_n$. Integrating at constant temperature and pressure ($dT = 0$, $dp = 0$), we obtain

$$\Phi = \mu_1 m_1 + \mu_2 m_2 + \ldots \mu_n m_n. \qquad (16)$$

If we desire to think of the total thermodynamic potential of a mixture as the sum of partial thermodynamic potentials of the various components of the mixture, then we may evidently say that the partial thermodynamic potential of unit mass of a component in the phase in question is equal to the chemical potential of that component.

System with Semi-Permeable Membranes

Let us now consider briefly a system of N components and P phases in which one of the phases, which we may call phase 1, is surrounded by a membrane or wall permeable to all the components but one, e.g., component 1. The temperature will be the same in all the phases, but in phase 1 the pressure p_1 may be different from the pressure p common to all the other phases. Equations (1) to (7) will still be valid for the system under consideration with this difference that in equation (6) we must write dp_1 for the first phase and dp for all the other phases. Moreover, equations (9) are valid but we have the additional condition that $\delta m_1' = 0$. Hence in equation (8) the term $\mu_1' \delta m'$ is necessarily zero and hence μ_1' may assume any value determined by T, p_1 and the composition of phase 1. For the sake of simplicity, let us suppose that our system consists of two phases only, phase 1 containing m_1' grams of salt and m_2' grams of water, whereas phase 2 consists entirely of m_2'' grams of water. The two phases are separated by a membrane permeable to water and the pressure on the solution is p_1 and on the pure water p. At equilibrium, the chemical potential of the water must be the same in the two phases or $\mu_2' = \mu_2''$. The chemical potential of the salt,

μ_1', will depend on T, p_1 and the ratio $\frac{m_1'}{m_2'}$. Can we determine whether p_1 is greater or less than p? From equation (6) we have for any phase

$$\left(\frac{d\Phi}{dp}\right)_{T,\, m_1,\, m_2} = V \quad \text{and} \quad \left(\frac{d\Phi}{dm_1}\right)_{T,\, v,\, m_2} = \mu_1.$$

Hence

$$\left(\frac{\partial^2 \phi}{\partial p\, \partial m_1}\right)_{T,\, m_2} = \left(\frac{dV}{dm_1}\right)_{T,\, v,\, m_2} = \left(\frac{d\mu_1}{dp}\right)_{T,\, m_1,\, m_2} \tag{17}$$

Now $\left(\frac{dV}{dm_1}\right)_{T,\, v,\, m_2}$ is the ratio of the increase in volume to the increase in the mass of component 1 when T, p, and m_2 are kept constant. This ratio we can safely take to be in general positive. Hence $\left(\frac{d\mu_1}{dp}\right)_{T,\, m_1,\, m_2}$ is positive; or, in words, the chemical potential of a component in a phase is increased when the pressure on the phase is increased. We shall make use of the experimental fact that the vapor pressure of a pure liquid at a fixed temperature is always diminished when any substance is dissolved in the liquid, even when the total pressure on the liquid is kept constant. Since the chemical potential of water in the vapor phase is always equal to its chemical potential in the liquid phase and since we have just seen that $\left(\frac{d\mu_1}{dp}\right)_{T,\, m_1,\, m_2}$ is positive, we conclude that the chemical potential of water in a solution is less than that of pure water at the same temperature and pressure. Hence returning to our system of a salt solution at temperature T and pressure p_1, separated by a semi-permeable wall from pure water at the same temperature but a different pressure p, we find that p_1 must be greater than p if the water is to have the same chemical potential in both phases. The difference in pressures $(p_1 - p)$ is usually called the osmotic pressure of the solution.

Some further information about the chemical potentials of substances may be obtained by the following considerations. On differentiating equation (16) completely and comparing the result

with equation (6), we obtain, for each phase of a system of two components,

$$\begin{aligned} d\Phi &= \mu_1\, dm_1 + \mu_2\, dm_2 + m_1\, d\mu_1 + m_2\, d\mu_2 \\ &= -S\, dT + V\, dp + \mu_1\, dm_1 + \mu_2\, dm_2. \end{aligned} \tag{18}$$

Hence,

$$m_1\, d\mu_1 + m_2\, d\mu_2 = -S\, dT + V\, dp. \tag{19}$$

From equation (18) we deduce that

$$\left(\frac{\partial^2 \phi}{\partial m_1\, \partial m_2}\right)_{T,\, p} = \left(\frac{d\mu_1}{dm_2}\right)_{T,\, p,\, m_1} = \left(\frac{d\mu_2}{dm_1}\right)_{T,\, p,\, m_2}. \tag{20}$$

Now we concluded on the basis of experience that the potential of a substance in a solution is diminished when the mass of another substance is increased, i.e., we assume it to be a general law that $\left(\frac{d\mu_1}{dm_2}\right)_{T,\, p,\, m_1}$ is negative. Now if in a phase containing the masses m_1 and m_2, the mass m_2 is increased by dm_2, while T, p and m_1 are kept constant, we have, from (19),

$$m_1 \left(\frac{d\mu_1}{dm_2}\right)_{T,\, p,\, m_1} + m_2 \left(\frac{d\mu_2}{dm_2}\right)_{T,\, p,\, m_1} = 0. \tag{21}$$

We shall suppose that in all cases the components are so selected that m_1 and m_2 are either zero or positive. This can always be done. Therefore, since $\left(\frac{d\mu_1}{dm_2}\right)_{T,\, p,\, m_1}$ is always negative, $\left(\frac{d\mu_2}{dm_2}\right)_{T,\, p,\, m_1}$ is necessarily positive. Hence we deduce that the chemical potential of a component increases when the mass of that component is increased in a phase otherwise unchanged. Now experiments on the lowering of the vapor pressure of liquids by dissolved substances go to show that $m_1 \left(\frac{d\mu_1}{dm_2}\right)_{T,\, p,\, m_1}$ is negative and approaches a constant value for small values of $\frac{m_2}{m_1}$. Hence as m_2 approaches zero, since $m_1 \left(\frac{d\mu_1}{dm_2}\right)_{T,\, p,\, m_1}$ remains finite and negative, $m_2 \left(\frac{d\mu_2}{dm_2}\right)_{T,\, p,\, m_1}$ must be finite and positive and hence $\left(\frac{d\mu_2}{dm_2}\right)_{T,\, p,\, m_1}$ approaches infinity as m_2 approaches zero.

Representing the value of $m_1\left(\frac{d\mu_1}{dm_2}\right)_{T, p, m_1}$ by $-A$ where A is positive, we have

$$\left(\frac{d\mu_1}{dm_2}\right)_{T, p, m_1} = -\frac{A}{m_1} = -\frac{m_2}{m_1}\left(\frac{d\mu_2}{dm_2}\right)_{T, p, m_1}. \tag{22}$$

Hence $$\left(\frac{d\mu_2}{dm_2}\right)_{T, p, m_1} = \frac{A}{m_2}. \tag{23}$$

On integration we find

$$\mu_2 = A \log m_2 + f(T, p, m_1), \tag{24}$$

or, since μ_2 is a function of T, p and $\frac{m_1}{m_2}$,

$$\mu_2 = A \log \frac{m_2}{m_1} + f(T, p), \tag{25}$$

where A may also be a function of T and p.

Changes from One Equilibrium State to Another

We have in this chapter discussed the conditions under which a system will remain in equilibrium if the temperature and pressure are maintained constant and we have found that in general the conditions are that the chemical potentials of the various components shall be the same in all phases. It is possible however to imagine a change to take place in the temperature, pressure, and the masses of the components in each phase leading to a new state of equilibrium. Thus we found, to take a simple case, water and water vapor to be in equilibrium at constant temperature and pressure when the thermodynamic potential of unit mass of the water is equal to that of unit mass of vapor or (see equation (16) and the discussion immediately following it) when the chemical potentials of the water and the vapor are equal. But we can raise the temperature and the pressure and still have water and water vapor in equilibrium.

We shall suppose then that our system of N components in P phases is in equilibrium, for given values of T, p, m_1', m_2', etc. We shall suppose that the system undergoes an actual infinitesimal change of state and we desire to know under what conditions

this new state is also a state of equilibrium at constant temperature and pressure. If Φ is the thermodynamic potential of our original system, $\Phi + d\Phi$ will represent that of the system in the new state. The condition that our original system should be in equilibrium at constant temperature and pressure was expressed by the equation

$$\delta\Phi = 0. \tag{26}$$

Similarly our new system will be in equilibrium at constant temperature and pressure if

$$\delta(\Phi + d\Phi) = 0, \tag{27}$$

or, since $\delta\Phi = 0$, the condition is

$$\delta\, d\Phi = 0. \tag{28}$$

Now for the first phase we have

$$d\Phi' = -S'\,dT + V'\,dp + \mu_1'\,dm_1' + \cdots + \mu_n'\,dm_n'. \tag{29}$$

Therefore for the whole system of P phases, if S and V are the total entropy and volume,

$$d\Phi = -S\,dT + V\,dp + \sum_1^P (\mu_1'\,dm_1' + \ldots \mu_n'\,dm_n'). \tag{30}$$

We must now find the value of a virtual variation in $d\Phi$, i.e., of $\delta\, d\Phi$, at constant temperature and pressure, and put the result equal to zero. We thus obtain

$$\delta\, d\Phi = -\delta S\,dT + \delta V\,dp + \sum_1^P (\delta\mu_1'\,dm_1' + \ldots \delta\mu_n'\,dm_n')$$
$$+ \sum_1^P (\mu_1'\,\delta\,dm_1' + \ldots \mu_n'\,\delta\,dm_n') = 0. \tag{31}$$

But the last term in (31) is zero since

$$\mu_1'\,\delta\,dm_1' + \mu_1''\,\delta\,dm_1'' + \ldots \mu_1^p\,\delta\,dm_1^p$$
$$= \mu_1'\delta\,(dm_1' + dm_1'' + \ldots dm_1^p)$$

since $$\mu_1' = \mu_1'' = \ldots \mu_1^p,$$

and this is equal to zero, since

$$m_1' + m_1'' + \ldots m_1^p = \text{constant}.$$

Hence we obtain the following condition that our system shall be in equilibrium at constant temperature and pressure in the new state:

$$-\delta S\, dT + \delta V\, dp + \sum_{1}^{P} (\delta\mu_1'\, dm_1' + \ldots \delta\mu_n'\, dm_n') = 0. \qquad (32)$$

And if we represent by Q the quantity of heat absorbed by the system in the virtual variation,

$$\delta S = \frac{Q}{T}$$

and equation (32) becomes

$$-\frac{Q}{T} dT + \delta V\, dp + \sum_{1}^{P} (\delta\mu_1\, dm_1' + \cdots + \delta\mu_n'\, dm_n') = 0. \qquad (33)$$

Application to Univariant Systems

For a univariant system, $F = N + 2 - P = 1$ and all the internal variables are functions of a single variable, say the temperature. If we imagine a virtual variation in such a system at constant temperature, all the internal variables, p, μ_1', μ_1'', etc., will remain unchanged, but there will be a quantity of heat Q absorbed and a change in volume δV. For such an isothermal expansion or compression of our univariant system, we obtain, since $\delta\mu$ is zero, $-\frac{Q}{T} dT + \delta V\, dp = 0$ or

$$Q = T\, \delta V \frac{dp}{dT} \quad \text{or} \quad \frac{dp}{dT} = \frac{Q}{T\, \delta V}. \qquad (34)$$

In any system with one degree of freedom, the equilibrium pressure and temperature are related according to equation (34). Whether the equilibrium pressure shall increase or decrease with rise in temperature depends on whether Q and δV have the same sign or not. The student will perceive that the Clapeyron-Clausius equation is a special case of equation (34). The Clapeyron formula refers to a univariant system of one component, whereas equation (34) holds for a univariant system of any number of components. Thus for a univariant system of one component, we have $F = N + 2 - P = 1 + 2 - P = 1$ or $P = 2$.

If m' and m'' are the masses of the one component in the two phases, and if v' and v'' are the specific volumes of the two phases, for any virtual isothermal change in which the mass $\delta m''$ goes from phase 1 to phase 2, we have, if λ is the heat absorbed per gram transferred,

$$Q = \lambda \delta m''; \quad \delta V = (v'' - v')\, \delta m''.$$

Hence from (34)

$$\lambda = T\,(v'' - v')\,\frac{dp}{dT},$$

identical with the Clapeyron equation ((28), Chap. X).

Univariant System of Two Components

In this case $N = 2$, $P = 3$. As an example, let us consider a system consisting of a solid salt (phase 1), an aqueous solution of the salt (phase 2), and water vapor (phase 3). Water will be component 1 and the salt component 2. Thus m_2' is the mass of solid salt, m_2'' the mass of salt in the solution, m_1'' the mass of water in the solution, and m_1''' is the mass of vapor. According to the phase rule, all the internal variables of this system are functions of a single variable, say the temperature; thus the pressure p and the ratio of salt to water in the liquid phase $\frac{m_2''}{m_1''} = r$ are functions of T only. For any virtual change, we have the conditions:

$$\delta m_2' + \delta m_2'' = 0 \quad \text{and} \quad \delta m_1'' + \delta m_1''' = 0.$$

Let us suppose that an infinitely small amount of water $\delta m_1''' = -\delta m_1''$, evaporates, isothermally, out of the solution and, since $r = \frac{m_2''}{m_1''}$ is constant, that simultaneously the quantity of salt $\delta m_2' = -\delta m_2''$ precipitates out of the solution. Since $r = \frac{m_2''}{m_1''}$, $\delta m_2'' = r\, \delta m_1''$, or $\delta m_2' = r\, \delta m_1'''$. If v', v'' and v''' are the specific volumes of the three phases,

$$\begin{aligned} \delta V &= v'\, \delta m_2' - v''\,(\delta m_2' + \delta m_1''') + v'''\, \delta m_1''' \\ &= rv'\, \delta m_1''' - v''\,(r + 1)\, \delta m_1''' + v'''\, \delta m_1''' \\ &= \delta m_1'''\,(v''' + rv' - (r + 1)\, v''). \end{aligned} \tag{35}$$

If λ_s is the heat absorbed when one gram of water evaporates isothermally from the liquid phase, then $Q = \lambda_s \delta m_1'''$. Hence from (34)

$$\lambda_s = T \frac{\delta V}{\delta m_1'''} \frac{dp}{dT} = T \frac{dp}{dT} (v''' + rv' - (r + 1) v''). \quad (36)$$

Now just as the Clapeyron formula was obtained in a modified form by assuming the vapor to be an ideal gas and neglecting the specific volume of the liquid, so in this case, if we neglect v' and v'' and write $v''' = \frac{RT}{Mp}$, we obtain

$$\lambda_s = \frac{RT^2}{M} \frac{d \log p}{dT}, \quad (37)$$

where λ_s is the heat absorbed when one gram of water is evaporated at constant temperature T and vapor pressure p from a saturated solution of a salt. The evaporation will be accompanied by the precipitation of a definite amount of salt. If we carry out the process in the reverse direction, we can say that λ_s is the heat evolved when one gram of water vapor and the requisite amount of solid salt form a saturated solution at constant temperature and pressure. We can find a relation between λ_s and h_s (the heat evolved when the requisite amount of salt dissolves in one gram of liquid water at the temperature T to form a saturated solution). The pressure at which this occurs is of minor importance, since the volume changes are slight. Let p_0 be the vapor pressure of pure water at the temperature T. Starting with one gram of water vapor at the temperature T and pressure p, let us compress the vapor isothermally to the greater pressure p_0. Assuming the vapor to be an ideal gas, its energy will not have changed. Let us now condense the gram of water vapor isothermally at the constant pressure p_0 to liquid water. The heat evolved is $\lambda = \frac{RT^2}{M} \frac{d \log p_0}{dT}$ and the work done on the system is $p_0 v_0$ if v_0 is the specific volume of the water vapor at pressure p_0. The decrease in the energy of the water is therefore $\lambda - p_0 v_0 = \lambda - \frac{R}{M} T$. Decreasing the pressure on the liquid water from p_0 to p does not change the energy appreciably. Now bring the gram

of water at T and p in contact with the requisite amount of solid salt. The heat evolved is h_s and no appreciable amount of work is done. The total loss in energy is therefore $\lambda - \frac{R}{M}T + h_s$. This must be the same as when the water vapor and salt are brought together directly, and in this case the total loss in energy is $\lambda_s - pv = \lambda_s - \frac{R}{M}T$. Accordingly since

$$\lambda - \frac{R}{M}T + h_s = \lambda_s - \frac{R}{M}T,$$

we obtain

$$h_s = \lambda_s - \lambda = \frac{RT^2}{M}\frac{d \log \frac{p}{p_0}}{dT}. \tag{38}$$

In other words, the heat h_s evolved when one gram of liquid water unites with a salt to form a saturated solution at a temperature T and a vapor pressure p is given by equation (38) where p_0 is the vapor pressure of pure water at the same temperature and p is the vapor pressure of the saturated solution.

Divariant Systems

According to the phase rule, in divariant systems, the number of phases is equal to the number of components. We shall discuss the important case of two components in two phases. The condition of equilibrium at constant temperature and pressure, as given by equation (33) becomes in this case

$$-\frac{Q}{T}dT + \delta V\,dp + \delta\mu_1'\,dm_1' + \delta\mu_1''\,dm_1'' + \delta\mu_2'\,dm_2' + \delta\mu_2''\,dm_2'' = 0. \tag{39}$$

We shall represent the composition of the first and second phases by the ratios r' and r'' where

$$r' = \frac{m_2'}{m_1'} \quad \text{and} \quad r'' = \frac{m_2''}{m_1''}. \tag{40}$$

For the first phase, we have

$$\delta\mu_1' = \left(\frac{d\mu_1'}{dm_1'}\right)_{T,p,m_2'}\delta m_1' + \left(\frac{d\mu_1'}{dm_2'}\right)_{T,p,m_1'}\delta m_2',$$

$$\delta\mu_2' = \left(\frac{d\mu_2'}{dm_1'}\right)_{T,p,m_2'}\delta m_1' + \left(\frac{d\mu_2'}{dm_2'}\right)_{T,p,m_1'}\delta m_2'. \tag{41}$$

Similar equations hold for $\delta\mu_1''$, $\delta\mu_2''$ of the second phase. Now from equation (19) we have, when T and p are constant,

$$\left.\begin{aligned} m_1'\left(\frac{d\mu_1'}{dm_1'}\right)_{T,p,m_2'} + m_2'\left(\frac{d\mu_2'}{dm_1'}\right)_{T,p,m_2'} &= 0, \\ m_1'\left(\frac{d\mu_1'}{dm_2'}\right)_{T,p,m_1'} + m_2'\left(\frac{d\mu_2'}{dm_2'}\right)_{T,p,m_1'} &= 0. \end{aligned}\right\} \quad (42)$$

Similar equations hold for the second phase. According to equations (20) and (22), for any phase,

$$\left(\frac{d\mu_1}{dm_2}\right)_{T,p,m_1} = \left(\frac{d\mu_2}{dm_1}\right)_{T,p,m_2} = -\frac{A}{m_1}, \quad (43)$$

where A is essentially positive. We can, therefore, write for our first phase,

$$\left(\frac{d\mu_1'}{dm_2'}\right)_{T,p,m_1'} = \left(\frac{d\mu_2'}{dm_1'}\right)_{T,p,m_2'} = -\frac{A'}{m_1'}, \quad (44)$$

and for the second phase

$$\left(\frac{d\mu_1''}{dm_2''}\right)_{T,p,m_1''} = \left(\frac{d\mu_2''}{dm_1''}\right)_{T,p,m_2''} = -\frac{A''}{m_1''}. \quad (45)$$

The partial derivatives in (41) may then be represented as follows, bearing equations (40) and (42) in mind:

$$\left(\frac{d\mu_1'}{dm_1'}\right)_{T,p,m_2'} = \frac{A'r'}{m_1'}; \qquad \left(\frac{d\mu_2'}{dm_2'}\right)_{T,p,m_1'} = \frac{A'}{m_2'}, \quad (46)$$

with similar expressions for the second phase. If our system in the new state (as represented by the changes in the variables, dT, dp, dm_1', dm_2', dm_1'', dm_2'') is to be in equilibrium at constant temperature and pressure, it must be in equilibrium as regards the transfer of each component separately from one phase to the second. We shall consider then the conditions that must be satisfied: firstly, if the first component is to be in equilibrium in both phases, and secondly, if the second component is to be in equilibrium in both phases. We shall therefore imagine two kinds of virtual changes, the first involving the transfer of the first component only and the second the transfer of the second

component only. For the first type of virtual variation, then, we have $\delta m_1'' = -\delta m_1'$ and $\delta m_2' = \delta m_2'' = 0$. For the transfer of the mass $\delta m_1''$, from the first phase to the second, let Q_1 be the heat absorbed and $\delta_1 V$ be the increase in volume. Then in this case, equation (39) becomes, bearing equations (41), (44), (45) and (46) in mind, and remembering that $\delta m_1'' = -\delta m_1'$, and that $\delta m_2' = \delta m_2'' = 0$,

$$-\frac{Q_1}{T}dT + \delta_1 V\,dp + \delta m_1''\left[\frac{A'}{m_1'}dm_2' - \frac{A'r'}{m_1'}dm_1' - \frac{A''}{m_1''}dm_2'' + \frac{A''r''}{m_1''}dm_1''\right] = 0. \quad (47)$$

From equation (40) we obtain

$$dr' = \frac{1}{m_1'}dm_2' - \frac{m_2'}{(m_1')^2}dm_1' = \frac{1}{m_1'}dm_2' - \frac{r'}{m_1'}dm_1'. \quad (48)$$

Hence equation (47) may be written

$$-\frac{Q_1}{T}dT + \delta_1 V\,dp + \delta m_1''\,[A'\,dr' - A''\,dr''] = 0. \quad (49)$$

If we define the quantities λ_1 and v_1 by the equations,

$$\lambda_1 = \frac{Q_1}{\delta m_1''}; \qquad v_1 = \frac{\delta_1 V}{\delta m_1''}, \quad (50)$$

we see that λ_1 and v_1 are the heat absorbed and the increase in volume respectively when one gram of component 1 goes from a large amount of phase 1 to a large amount of phase 2 at constant temperature and pressure. Thus we may write equation (49) in the form,

$$-\frac{\lambda_1}{T}dT + v_1\,dp + A'\,dr' - A''dr'' = 0. \quad (51)$$

For the second type of virtual variation we have $\delta m_1'' = \delta m_1' = 0$ and $\delta m_2'' = -\delta m_2' > 0$. In this case, let Q_2 be the heat absorbed and $\delta_2 V$ the increase in volume accompanying the transfer of the quantity $\delta m_2''$ of the second component from phase 1 to phase 2. Also let λ_2 and v_2 be defined, analogously to λ_1 and v_1, by the equations

$$\lambda_2 = \frac{Q_2}{\delta m_2''}; \qquad v_2 = \frac{\delta_2 V}{\delta m_2''}. \quad (52)$$

Just as we obtained equation (51) for the first type of virtual variation, so we can obtain for the second type

$$-\frac{\lambda_2}{T}dT + v_2\,dp - \frac{A'}{r'}dr' + \frac{A''}{r''}dr'' = 0. \tag{53}$$

If our system is in equilibrium at constant temperature and pressure for given values of T, p, r' and r'', and if we change our system into the new state, the changes being represented by dT, dp, dr' and dr'', then if the new state is to be one of equilibrium, there are two conditions, (51) and (53), which must be satisfied. Hence of the four variables, T, p, r', r'', only two can be varied arbitrarily and hence, in harmony with the phase rule, our system has two degrees of freedom.

It is often convenient to have the equations which we have just developed based on moles instead of grams as the unit of mass of each component and we shall obtain the corresponding equations in the important case that one of the two phases considered is gaseous. The other phase may be liquid or solid but for the sake of clearness we shall suppose it to be liquid. In the liquid phase we may suppose that we have N_1 moles of component 1 and N_2 moles of component 2. In the vapor phase let the mole numbers be n_1 and n_2. Moreover we shall make use of the mole fractions, defined by the equations:

$$\left.\begin{aligned} x_1 &= \frac{N_1}{N_1 + N_2}, & x_2 &= \frac{N_2}{N_1 + N_2}, \\ y_1 &= \frac{n_1}{n_1 + n_2}, & y_2 &= \frac{n_2}{n_1 + n_2}. \end{aligned}\right\} \tag{54}$$

Instead of the ratios of the masses, r' and r'', we shall employ the ratios of the mole numbers; thus, corresponding to r' and r'', we shall have $\frac{N_2}{N_1} = \frac{x_2}{x_1}$ and $\frac{n_2}{n_1} = \frac{y_2}{y_1}$. Instead of μ, the chemical potential of one gram of a component, we shall use the symbol Φ for the potential of one mole. And instead of A' and A'' of equations (44) and (45), we shall use B' and B'' defined by the equations:

$$\left.\begin{aligned} \left(\frac{d\Phi_1'}{dN_2}\right)_{T,\,v,\,N_1} &= \left(\frac{d\Phi_2'}{dN_1}\right)_{T,\,v,\,N_2} = -\frac{B'}{N_1}. \\ \left(\frac{d\Phi_1''}{dn_2}\right)_{T,\,v,\,n_1} &= \left(\frac{d\Phi_2''}{dn_1}\right)_{T,\,v,\,n_2} = -\frac{B''}{n_1}. \end{aligned}\right\} \tag{55}$$

In place of $\lambda_1, v_1, \lambda_2, v_2$ of equations (50) and (52) which refer to one gram of the components, we shall use L_1, V_1, L_2, V_2 based on moles as the unit. Thus we shall have corresponding to the equations (51) and (53), the two following:

$$-\frac{L_1}{T}dT + V_1 dp + B'd\left(\frac{N_2}{N_1}\right) - B''d\left(\frac{n_2}{n_1}\right) = 0. \quad (56)$$

$$-\frac{L_2}{T}dT + V_2 dp - \frac{N_1}{N_2}B'd\left(\frac{N_2}{N_1}\right) + \frac{n_1}{n_2}B''\,d\left(\frac{n_2}{n_1}\right) = 0. \quad (57)$$

Assuming the vapor phase to be an ideal gas mixture, in which the partial pressures are p_1 and p_2 and the total pressure p, we have for the total volume V of the vapor phase

$$V = (n_1 + n_2)\frac{RT}{p}.$$

Now

$$V_1 = \left(\frac{dV}{dn_1}\right)_{T,\,p,\,n_2} = \frac{RT}{p} \quad \text{and} \quad V_2 = \left(\frac{dV}{dn_2}\right)_{T,\,p,\,n_1} = \frac{RT}{p}.$$

Let $U_1, U_2, S_1, S_2, \Phi_1'', \Phi_2''$ be the energy, entropy and potential per mole of gases 1 and 2 at the temperature T and total pressure p. According to equation (15) (Chap. VIII)

$$S_1 = C_{p_1}\log T - R\log p + k_1 - R\log\frac{n_1}{n_1 + n_2}. \quad (58)$$

Since $\Phi_1'' = U_1 - TS_1 + p_1V$ and since $p_1V = RT$,

$$\Phi_1'' = U_1 - C_{p_1}T\log T + RT\log p - k_1T + RT$$

$$+ RT\log\frac{n_1}{n_1 + n_2} = f(T, p) + RT\log\frac{n_1}{n_1 + n_2}. \quad (59)$$

Hence

$$\left(\frac{d\Phi_1''}{dn_2}\right)_{T,\,p,\,n_1} = -\frac{RT}{n_1 + n_2} \quad (60)$$

and therefore, from equations (55),

$$B'' = \frac{n_1}{n_1 + n_2}RT = y_1RT = \frac{p_1}{p}RT. \quad (61)$$

We may therefore, since $\frac{n_2}{n_1} = \frac{p_2}{p_1}$, write equations (56) and (57) as follows:

$$\left.\begin{aligned} -\frac{L_1}{T}dT + \frac{RT}{p}dp + B'd\left(\frac{N_2}{N_1}\right) - \frac{p_1}{p}RT\,d\left(\frac{p_2}{p_1}\right) = 0, \\ -\frac{L_2}{T}dT + \frac{RT}{p}dp - \frac{N_1}{N_2}B'd\left(\frac{N_2}{N_1}\right) + \frac{p_1}{p_2}\cdot\frac{p_1}{p}RT\,d\left(\frac{p_2}{p_1}\right) = 0. \end{aligned}\right\} \quad (62)$$

Since $dp = dp_1 + dp_2$ and since $d\left(\frac{p_2}{p_1}\right) = \frac{dp_2}{p_1} - \frac{p_2\,dp_1}{p_1^2}$, equations (62) may be transformed into the following, bearing in mind that $\frac{N_2}{N_1} = \frac{x_2}{x_1} = \frac{1 - x_1}{x_1}$ and that therefore $d\left(\frac{N_2}{N_1}\right) = d\left(\frac{1 - x_1}{x_1}\right) = -\frac{dx_1}{x_1^2}$,

$$\left.\begin{aligned} -\frac{L_1}{T}dT + RT\frac{dp_1}{p_1} - \frac{B'}{x_1^2}dx_1 = 0, \\ -\frac{L_2}{T}dT + RT\frac{dp_2}{p_2} + \frac{B'}{x_1x_2}dx_1 = 0. \end{aligned}\right\} \quad (63)$$

Equations (63) may also be written

$$\left.\begin{aligned} -L_1\,d\log T + RT\,d\log p_1 - \frac{B'}{x_1}d\log x_1 = 0, \\ -L_2\,d\log T + RT\,d\log p_2 + \frac{B'}{x_2}d\log x_1 = 0. \end{aligned}\right\} \quad (64)$$

The Duhem-Margules Equation

If the liquid phase is supposed to undergo a slight change in composition at constant temperature, there will be changes in the partial vapor pressures p_1 and p_2. Since $dT = 0$, we have, from (64),

$$\left.\begin{aligned} x_1\left(\frac{d\log p_1}{dx_1}\right)_T = \frac{B'}{x_1RT}, \\ x_2\left(\frac{d\log p_2}{dx_1}\right)_T = -\frac{B'}{x_1RT}. \end{aligned}\right\} \quad (65)$$

Hence we have the Duhem-Margules equation

$$\left.\begin{aligned} x_1\frac{d\log p_1}{dx_1} + x_2\frac{d\log p_2}{dx_1} = 0, \\ \text{or} \qquad x_1\frac{d\log p_1}{dx_1} = x_2\frac{d\log p_2}{dx_2}, \end{aligned}\right\} \quad (66)$$

We see that the value of B' can be determined by equations (65) if p_1 or p_2 are known as functions of the composition of the liquid mixture. We also see that if p_1 is known as a function of the composition, then p_2 can be determined.

Distillation at Constant Pressure

Assume phase 1 = liquid, phase 2 = vapor. If in equations (51) and (53) we set $dp = 0$, the new equilibrium state is at the same pressure as the original one. Under these circumstances, we can deduce from equations (51) and (53), the following:

$$\left.\begin{aligned} dr' &= \frac{r'(\lambda_1 + r''\lambda_2)}{A'(r' - r'')} \cdot \frac{dT}{T}, \\ dr'' &= \frac{r''(\lambda_1 + r'\lambda_2)}{A''(r' - r'')} \cdot \frac{dT}{T}. \end{aligned}\right\} \tag{67}$$

Hence

$$\frac{dr'}{dr''} = \frac{A''r'(\lambda_1 + r''\lambda_2)}{A'r''(\lambda_1 + r'\lambda_2)}. \tag{68}$$

Since all the terms in the expression on the right hand side are positive, $\frac{dr'}{dr''}$ is positive. Hence in distilling a mixture of two components at constant pressure, the concentrations of the two phases change in the same sense. If we define the more volatile component as the one which is present in the second phase in greater proportion than in the first phase, and if we call it the second component, then with this understanding $r'' > r'$. Hence from (67) and (68), as the distillation proceeds, both r' and r'' diminish. The two equations (67) may also be written

$$\frac{dT}{dr'} = \frac{A'T(r' - r'')}{r'(\lambda_1 + r''\lambda_2)}; \qquad \frac{dT}{dr''} = \frac{A''T(r' - r'')}{r''(\lambda_1 + r'\lambda_2)}. \tag{69}$$

It may happen that at a definite stage in the distillation at constant pressure, r' becomes equal to r'', that is, the two phases become identical in composition. At this point $\frac{dT}{dr'} = 0$, and T has a maximum or minimum value, and the boiling-point is constant. Now since in distillation at constant pressure, any change in temperature must be zero or positive, the boiling-point will be

actually constant only when it represents a maximum value. For if some slight variation takes the system away from the state in which T has its maximum value, further heating will bring it back to this state; whereas if a system departs in the least from a state corresponding to a minimum boiling-point, further heating will remove it still farther from that state.

Isothermal Distillation

If we put $dT = 0$ in equations (51) and (53), we obtain the following relations:

$$\left.\begin{aligned} dr' &= \frac{r'(v_1 + r''v_2)}{A'(r'' - r')}\,dp, \\ dr'' &= \frac{r''(v_1 + r'v_2)}{A''(r'' - r')}\,dp, \\ \frac{dr'}{dr''} &= \frac{A''r'(v_1 + r''v_2)}{A'r''(v_1 + r'v_2)}. \end{aligned}\right\} \tag{70}$$

Again $\frac{dr'}{dr''}$ is positive and therefore the compositions of both phases change in the same sense. Since the evaporation at constant temperature is accompanied by a diminution in pressure, dp is negative and hence since $r'' > r'$, dr' and dr'' are negative. Again, since

$$\left(\frac{dp}{dr'}\right)_T = \frac{A'(r'' - r')}{r'(v_1 + r''v_2)}, \tag{71}$$

it may happen that $r'' = r'$ at a certain stage and hence p will have a maximum or minimum value and we should have our system evaporating at constant pressure without any change in the composition of either phase. It is easy to show that it is only when p is a minimum that the system will in actual practice continue to evaporate at constant pressure.

The meaning of equations (51) and (53), which give the conditions of equilibrium between two phases in a system of two components, has been illustrated by supposing that the two phases are liquid and gaseous respectively. They hold however no matter what the state of aggregation of the phases may be. Thus they may be applied in a study of the melting-points of a mixture of two components or the equilibrium between two liquid

phases of two components. Examples of such cases will be considered later. We shall discuss briefly the equilibrium in a divariant system of two components in which one of the components is confined to one of the two phases. As examples we might mention the following systems: ice and an aqueous salt solution; salt and an aqueous solution of the salt; an aqueous salt solution and water vapor. For the sake of clearness we shall suppose that the first component is present in both phases and that the solution is the first phase. Thus if our system consists of a salt solution and water vapor, water is the first component and the solution is the first phase. We shall also in this case refer to the water as the "solvent" and to the salt as the "solute." Let m_1' and m_2' be the masses of water and salt in the solution, and m_1'' the mass of water vapor, and let $r = \frac{m_2'}{m_1'}$. Since we assume that the salt cannot pass into the vapor phase, equation (53) finds no application and we are left with (51) which in this case we shall write

$$-\frac{\lambda}{T}dT + v\,dp + A\,dr = 0, \tag{72}$$

where λ and v are defined by equations (50) and A by equation (44). Our system, which is in equilibrium for given values of T, p and r, will be in equilibrium for infinitesimal changes in T, p and r, if equation (72) is satisfied.

Change at Constant Concentration

If r is kept constant, we have

$$\left(\frac{dp}{dT}\right)_r = \frac{\lambda_r}{Tv}, \tag{73}$$

where λ_r is the latent heat of evaporation of one gram of water from an infinite amount of the solution of composition r and v is the corresponding increase in volume. If we assume that the vapor is an ideal gas and neglect the change in volume of the solution in comparison with that of the vapor, we can put $v = \frac{RT}{M_1 p}$ and hence

$$\left(\frac{dp}{dT}\right)_r = \frac{\lambda_r M_1 p}{RT^2} \quad \text{or} \quad \lambda_r = \frac{RT^2}{M_1}\left(\frac{d\log p}{dT}\right)_r. \tag{74}$$

λ_r is also the heat evolved when one gram of water vapor at pressure p and temperature T is condensed and unites with an infinite amount of the solution of composition r. We can carry out this process in a different manner. Starting with one gram of water vapor at T and p, we compress it isothermally to the pressure p_0, that of pure water at the temperature T. This process does not change the energy of the water vapor supposed to be an ideal gas. Then we condense the gram of water vapor at constant T and p_0 into liquid water. The decrease in energy is $\lambda - p_0 v_0 = \lambda - \frac{R}{M_1} T$. We decrease the pressure on the liquid water to p. This process is accompanied by a negligible change in energy. Then we add the gram of water to an infinite amount of the solution of composition r. The loss in energy is essentially equal to the heat evolved, which we shall denote by h_d and which is the differential heat of dilution per gram of water (compare Chap. VI). The total decrease in energy is therefore $\lambda - \frac{R}{M_1} T + h_d$. Now when the vapor is condensed directly into the solution, the loss in energy is $\lambda_r - pv = \lambda_r - \frac{R}{M_1} T$. Hence we find,

$$h_d = \lambda_r - \lambda, \tag{75}$$

or, from equation (31) of Chap. X and equation (74),

$$h_d = \frac{R}{M_1} T^2 \left(\frac{d \log \frac{p}{p_0}}{dT} \right)_r, \tag{76}$$

which is Kirchhoff's formula for the differential heat of dilution. This formula is very similar in appearance to equation (38) but in reality is quite different. The p of (38) refers to the vapor pressure of a solution which is maintained saturated, so that p is a function of the temperature alone. In (76), p is a function of both T and r.

In Chap. VI, we mentioned the fact that the heat of dilution tends to zero when the quantity of solvent is sufficiently great. When this is the case, $h_d = 0$ and hence $\left(\frac{d \log \frac{p}{p_0}}{dT} \right)_r = 0$ or $\log \frac{p}{p_0}$

$\left(\text{and therefore } \frac{p}{p_0}\right)$ is independent of the temperature. This is von Babo's Law and we accordingly see that von Babo's Law can only hold for solutions so dilute that the heat of dilution is negligible.

Change at Constant Temperature

In this case, equation (72) becomes

$$\left(\frac{dp}{dr}\right)_T = -\frac{A}{v}, \tag{77}$$

or if we assume the ideal gas laws for the vapor,

$$\left(\frac{d \log p}{dr}\right)_T = -\frac{M_1 A}{RT}. \tag{78}$$

Hence the vapor pressure of a solution at constant temperature diminishes as the concentration of the solute increases. Writing (78) in the form $\frac{dp}{p} = \left(-\frac{M_1 A}{RT}\right) dr$, we may assume that for small changes in r, $-\frac{M_1 A}{RT}$ is virtually constant and therefore

$$\frac{\Delta p}{p} = -k \cdot \Delta r. \tag{79}$$

If p_0 is the vapor pressure of the pure solvent ($r = 0$), then, for small values of r, we may write

$$\left(\frac{p_0 - p}{p_0}\right)_T = kr, \tag{80}$$

or the relative lowering of the vapor pressure is proportional to the concentration (Wüllner's Law).

Change at Constant Pressure

Equation (72) becomes, when $dp = 0$,

$$\left(\frac{dT}{dr}\right)_p = \frac{AT}{\lambda_r}, \tag{81}$$

or the boiling-point of a solution at constant pressure increases with the concentration of the (involatile) solute, since A, T and λ_r are positive. For small values of r, it can be shown that the elevation in the boiling-point is proportional to r.

Liquid and Solid Phases

If the second phase is solid, instead of gaseous, we shall have, for example, a salt solution in contact with ice. The application of equation (72) to this case follows readily from our preceding discussion. Equations (73), (77) and (81) apply without change when the appropriate interpretation is given to the symbols. Thus in (81) λ_r will represent the heat absorbed when one gram of water is frozen from a large amount of solution of concentration r. Since in general heat is actually evolved under these circumstances, λ_r will be negative and therefore $\left(\frac{dT}{dr}\right)_p$ of equation (81) will be negative. In other words, the freezing-point of a solution at constant pressure is lowered by increasing the concentration of the solute. Instead of ice as the second phase, we may have salt, so that our system consists of salt and a saturated solution of salt. Under these circumstances the results we have obtained apply without any modification if we call the salt the first component and therefore the solvent and the water the second component and therefore the solute. The symbol r will mean the ratio of water to salt in the first phase. Let us see the significance of equation (81) in this case. λ_r is the heat absorbed when one gram of salt separates out of an infinite amount of solution whose composition is 1 gram of salt to r grams of water. Writing equation (81) in the form

$$dr = \frac{\lambda_r}{AT}\,dT, \ (p = \text{constant}), \tag{82}$$

we see that if λ_r is positive, the concentration of the water increases and therefore the concentration of the salt decreases with rise in temperature. The concentration of salt in a saturated solution increases with rise in temperature if heat is absorbed when salt dissolves in a nearly saturated solution.

The usefulness of equations (73), (77), and (81) is somewhat impaired by the fact that the value of A is in general not known as an explicit function of T, p, m_1 and m_2. In a later chapter we shall show how the value of A can be determined in the case of ideal gases and dilute solutions and we shall then be able to put our equations in a much simpler form.

PROBLEMS

1. How many components are there in a system made up of water, sodium chloride and barium chloride?

2. How many components are there in a system made up of nitrogen, hydrogen and ammonia (*a*) at ordinary temperatures, (*b*) at 500° C.?

3. At 1000° C. the following reactions take place readily: $C + CO_2 \rightleftarrows 2\ CO$ and $CO_2 + H_2 \rightleftarrows CO + H_2O$. If a system at 1000° C. contains C, CO, CO_2, H_2 and H_2O, how many components and how many degrees of freedom are there?

4. How many components are there in an aqueous solution of cane-sugar if we suppose that in the solution the following reaction occurs: $C_{12}H_{22}O_{11} + m\ H_2O \rightleftarrows C_{12}H_{22}O_{11} \cdot m\ H_2O$?

5. The heat of solution at 18° C. of a grams of water and b grams of $NaNO_3$ is $\dfrac{-23.061\ b\ (b + 0.8791\ a)}{(b + 0.3261\ a)}$. The solution is saturated at 18° C. with respect to the salt when $\dfrac{b}{a} = 0.8665$. Calculate the heat evolved when 1 gram of water and 0.8665 gram of $NaNO_3$ form a saturated solution and from equation (38) find the value of $\dfrac{d \log \dfrac{p}{p_0}}{dT}$. Calculate the heat evolved when 1 gram of water is added to an infinite amount of the saturated solution and from equation (76) calculate the value of $\left(\dfrac{d \log \dfrac{p}{p_0}}{dT}\right)_{r = 0.8665}$.

6. Interpret equation (73) in the case of a salt solution in contact with ice. What in general are the signs of the quantities λ_r and v? Hence deduce a general rule for the change in the freezing-point of a solution with change in pressure.

7. Interpret equation (73) when we have a salt solution in contact with the solid salt. What are the signs of λ_r and v? If the pressure on a saturated solution of a salt in contact with the solid salt is increased, how must the temperature be changed if the composition of the solution is to remain unchanged?

8. Interpret equation (77) when the system consists of a salt solution and ice. How will increase in pressure at constant temperature affect the composition of the solution?

9. Interpret equation (77) when the system consists of a salt solution in contact with the solid salt. Deduce therefrom a general rule for the relation between the solubility of a salt and the pressure.

CHAPTER XII

APPLICATIONS OF THE PHASE RULE I

Systems of One Component

According to the phase rule, $F = N + 2 - P$, we have for a one-component system $F = 3 - P$. Since the number of degrees of freedom cannot be negative, we may have in our system one, two or three phases coexisting. Also, since the number of degrees of freedom cannot in this case be greater than two, we can represent the behavior of the system on an ordinary Cartesian diagram, taking the pressure and the temperature as independent variables. In the case of a system consisting of water, we shall have some such diagram as Fig. 14 if we confine our attention at present to ordinary ice as the only solid phase.

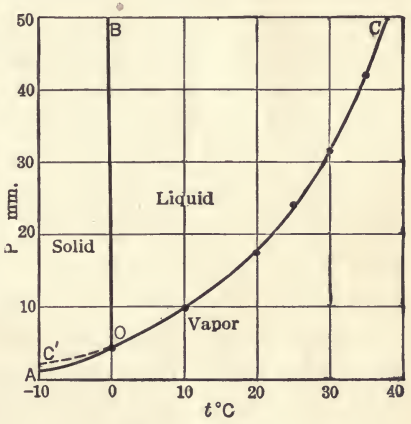


FIG. 14. Water

One Phase. Divariant System. Since $F = 2$, the variables p and t may be varied independently and hence the field of existence of a single phase will be represented by an area. Thus, in the area AOB, the solid exists; in the area BOC, the liquid; and in the area AOC, the vapor. The areas will be bounded by curves which represent the equilibrium between any pair of phases.

Two Phases. Univariant System. $F = 1$. Since there is but one independent variable, a change in pressure will bring with it a definite change in temperature so that the coexistence of two phases is represented by a curve. Thus for ice and vapor, we have the equilibrium curve AO; for ice and liquid water, the

curve BO; and for water and vapor, the curve CO. The general direction of these curves may be deduced from the Clapeyron formula, viz.: $\frac{dp}{dT} = \frac{\lambda}{T(v_2 - v_1)}$ in which λ is the heat absorbed when one gram of phase 1 is transferred to phase 2. If the vapor phase is the second phase, $\frac{dp}{dT}$ is necessarily positive, hence the curves AO and OC rise as the temperature increases. Since water is denser than ice, the curve OB slopes to the left as the pressure increases. The curve OC ends at C, the critical point.

Three Phases. Invariant System. $F = 0$. This state must be represented by a point where all three phases coexist and where the curves meet. It is easy to show that the curves must intersect at the same point. The coördinates of this point, point O in the diagram, are $p = 4.579$ mm. and $t = +0.0075°$ C. The equilibrium states so far described have been stable ones. We can, as we pointed out in Chap. IX, have states of a lower degree of stability. Thus water and vapor may coexist in states represented by points on the curve OC', although the most stable state under these circumstances is ice. We say that water and vapor in this case are in a state of metastable or labile equilibrium. The student can deduce from the Clapeyron formula the slopes of the curves AO and OC at the point O and hence show that the vapor pressure of water below zero is greater than that of ice at the same temperature.

The researches of Tammann * and of Bridgman † have shown that water can exist in at least five different crystalline forms, all of which, with the exception of ordinary ice (Ice I), are denser than water. The forms are designated as Ice I, Ice II, Ice III, Ice V and Ice VI. The absence of the term Ice IV is due to the fact that Tammann obtained some indications of a form which he called Ice IV, the existence of which is however still doubtful. The relationships of the various forms will be clear from diagram 15.

* Ann. der Physik, [4], **2**, 1424 (1900).
† Proc. Amer. Acad., **47**, 441 (1912).

The coördinates of some of the points in Fig. 15 are as follows:

Phases	Point	t	p
Ice I, liquid, vapor.....	O	+0.0075	4.579 mm. Hg.
Ice I, liquid, Ice III.....	C	−22° C	2115 $\frac{\text{kgms}}{\text{cm.}^2}$
Ice III, liquid, Ice V.....	D	−17° C.	3530 "
Ice V, liquid, Ice VI.....	E	+0.16° C.	6380 "
Ice I, Ice II, Ice III.....	F	−34.7° C.	2170 "
Ice II, Ice III, Ice V.....	G	−24.3° C.	3510 "

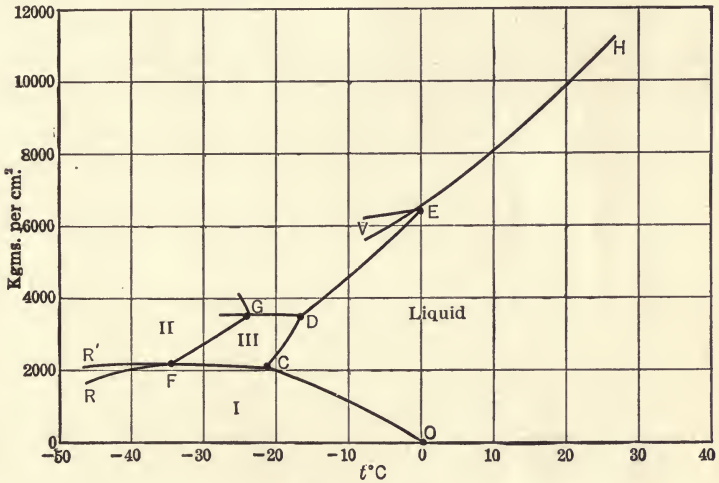


FIG. 15. Water

Triple Points

A system of one component has no degrees of freedom when three phases coexist. A point in a diagram such as Fig. 14 or 15 which represents such an invariant system is frequently called a triple point.

Transition Temperature

The temperature at which one phase is in equilibrium with a second is in general called a transition temperature. The name is usually applied however only when the phases are solid or liquid. This temperature, as we have seen, is a function of the pressure and sometimes of other variables. Thus 0° C. is the

transition temperature for the two phases, ice and water, at a pressure of one atmosphere. The term is still oftener applied to the equilibrium between two solid phases. Thus we should speak of the transition temperature of Ice I and Ice III under a given pressure and this would refer to some point on the curve *FC* in Fig. 15.

Sulphur

Sulphur exists in two solid forms, orthorhombic and monoclinic, in a vapor state and in a liquid state. The *p-T* diagram for sulphur is shown in Fig. 16.

Applying the phase rule, we see that, in a system consisting of sulphur, three is the largest number of phases which can coexist

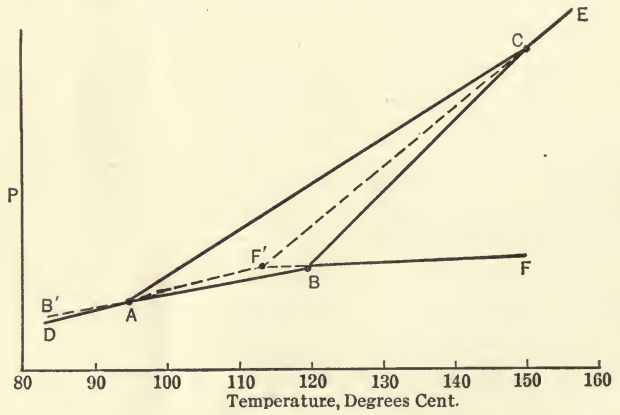


FIG. 16. Sulphur

in equilibrium. The curve *DA* is the vapor pressure curve of orthorhombic sulphur. The point *A* is a triple point where orthorhombic, monoclinic and vapor coexist under the pressure of the vapor. If the pressure is increased considerably, rhombic and monoclinic sulphur will remain in equilibrium if the temperature is raised in accordance with the curve *AC*. Since rhombic and monoclinic sulphur do not differ very much in density, it will require a very great increase in pressure to change the transition temperature appreciably. Thus the transition temperature under the vapor pressure of the sulphur is only slightly less than when

the pressure is one atmosphere. (Compare the change in freezing-point of water with the pressure.) Thus the transition temperature of the two solid forms of sulphur at atmospheric pressure will still be close to 95.5° C. The change from orthorhombic to monoclinic sulphur is so slow that orthorhombic sulphur can exist for some time at atmospheric pressure above 95.5°. The curve AF' is thus the vapor pressure curve of orthorhombic sulphur in labile equilibrium. F' is the point where rhombic sulphur, vapor and liquid coexist. The temperature corresponding to this is 114°. The curve $F'C$ represents the labile equilibrium between rhombic and liquid. Similarly, AB is the vapor pressure curve of monoclinic and B is the triple point for monoclinic, vapor and liquid. Along BC, monoclinic and liquid are in equilibrium, the point B representing approximately the ordinary melting-point of monoclinic sulphur (120° C.). The curve CE (of which $F'C$ is the labile continuation) represents the states of stable equilibrium between rhombic and liquid.

Divariant Systems: One Phase

Vapor Phase	Area $DABF$
Rhombic	Area $DACE$
Monoclinic	Area ABC
Liquid	Area $FBCE$

Univariant Systems: Two Phases

Rhombic-Vapor	Stable, Curve DA
	Labile, Curve AF'
Monoclinic-Vapor	Stable, Curve AB
	Labile, Curve AB'
Rhombic-Monoclinic	Stable, Curve AC
Rhombic-Liquid	Stable, Curve CE
	Labile, Curve CF'
Monoclinic-Liquid	Stable, Curve BC
Liquid-Vapor	Stable, Curve BF
	Labile, Curve BF'

Invariant Systems: Three Phases

Rhombic-Monoclinic-Vapor.....	Stable, Point A
Monoclinic-Vapor-Liquid.....	Stable, Point B
Rhombic-Monoclinic-Liquid.....	Stable, Point C
Rhombic-Liquid-Vapor.....	Labile, Point F'.

Two-Component Systems

The number of possible phases in a two-component system is sometimes rather large. Thus in the system $CaCl_2$ and H_2O, the following solid phases are known: Ice, $CaCl_2$, $CaCl_2 \cdot H_2O$, $CaCl_2 \cdot 2\,H_2O$, $CaCl_2 \cdot 4\,H_2O\ \alpha$, $CaCl_2$, $4\,H_2O\ \beta$, $CaCl_2 \cdot 6\,H_2O$. In addition we have the liquid phase and the gaseous phase. The study of two-component systems is made more complicated by the fact that we frequently have to do with liquids that are immiscible or only partially miscible, and with solids that may form solid solutions. It will, therefore, be impossible to go into detail in connection with the numerous types of systems. We must be content with a discussion of the characteristics of what may be considered as the principal types of two-component systems. And we shall begin with a study of the equilibrium between vapor and liquid phases, where the liquid phase may contain either component in any proportion whatever; i.e., the two components as liquids are miscible in all proportions over a certain range of temperatures and pressures. The thermodynamic foundation for our study of such systems is given in Chap. XI, to which reference should be made by the reader. Adopting the nomenclature of Chap. XI, the internal state of the system is a function of any two of the variables, T, p, r', r'', since our system has two degrees of freedom. We shall call T the boiling-point and p the vapor pressure. Evidently, then, T is a function of p and r' or of p and r'' and similarly p is a function of T and either r' or r''. If we maintain the pressure constant at some arbitrary value, the boiling-point, T, may be considered as a function of the composition of either phase; and similarly if the temperature is maintained constant, the vapor pressure will be determined by the composition of either phase. Thus we may represent the composition of either phase by the abscissæ in a

rectangular system of coördinates, and either the pressures at constant temperature or the boiling points at constant pressure by the ordinates.

Isothermal Distillation

The vapor pressure curves of a mixture of two liquids are of three types. In type I, the vapor pressures of all mixtures are intermediate between those of the pure components at the same temperature. Methyl alcohol and water give vapor pressure curves which are practically of this type. In type II, there is a certain mixture whose vapor pressure is less than that of all other mixtures and of either of the pure components. In type III, we

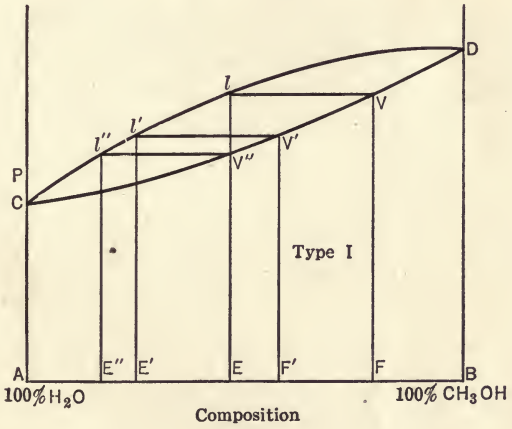


FIG. 17

meet with a mixture which has the maximum vapor pressure.

In Chap. XI we adopted the convention that the component which is present in the vapor phase in greater proportion than in the liquid phase is to be called the more volatile component. We also called it the second component, so that we had the relation $r'' > r'$. Since the pressure falls on isothermal expansion or distillation, both r'' and r' also decrease. Thus, in a system consisting of the two components, water and methyl alcohol in two phases, liquid and vapor, the percentage of alcohol is greater in the vapor phase than in the liquid phase and the percentage in both phases diminishes on isothermal distillation. In Fig. 17,

we have a diagrammatic representation of the vapor pressures of all possible mixtures of water and methyl alcohol at a fixed temperature. Since the vapor pressure can be expressed as a function of the composition of either phase, we shall have two curves, giving the relation between the pressure and the composition of both phases. Since the vapor phase is relatively richer in the more volatile component, the curve whose abscissæ refer to the composition of the vapor phase will be closer to the ordinate *BD* representing 100 per cent of the more volatile component. Thus, in Fig. 17, a liquid phase whose composition is *E* is in equilibrium with a vapor phase whose composition is represented

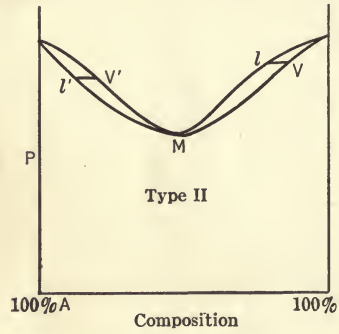


FIG. 18

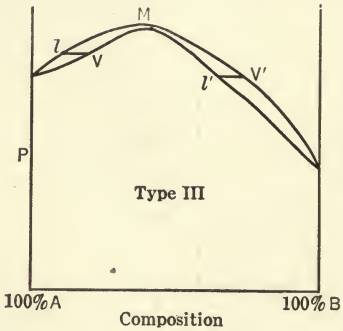


FIG. 19

by *F*. By determining where a horizontal line cuts the two curves, we can ascertain the composition of the two phases in equilibrium. It will be noticed that the composition of the phases in these diagrams is expressed in percentages and not by r' or r'', the ratio of the mass of the second component to that of the first. This is done to simplify the task of representing all possible compositions. The relation between r and the percentage composition is of course a very simple one. From equations (70) and (71) (Chap. XI) we deduced certain results which in the present case may be stated as follows: on isothermal distillation of a liquid of composition *E*, we shall obtain at first a vapor of composition *F*. As distillation proceeds, the composition of the liquid will change to E' and that of the vapor to F'. If all of the vapor remains in the system, the last drop of liquid evapo-

rating will have the composition E'' and the vapor (since it now contains all the original substances) will have the composition E. By fractional distillation, it would be possible to separate the mixture into the two components, water and methyl alcohol. Diagrams for pairs of liquids belonging to types II and III are given in Figs. 18 and 19.

Chloroform and acetone give a mixture belonging to type II whereas water and propyl alcohol belong to type III. The behavior of these mixtures on isothermal distillation can be readily deduced from the appropriate vapor pressure diagram.

Distillation at Constant Pressure

Since liquids are usually distilled at constant pressure, it will be worth while to study this part of our subject in some detail. Corresponding to the three types of vapor pressure curves, we shall have three kinds of boiling-point curves. In type I, the

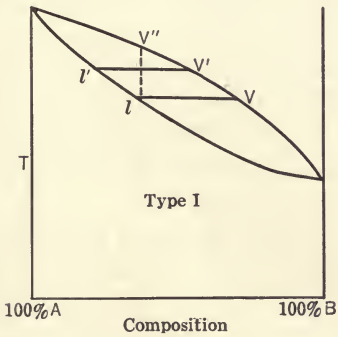


FIG. 20

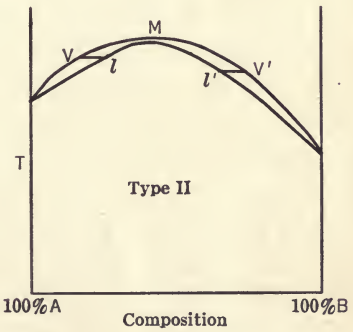


FIG. 21

boiling-points of the mixtures are intermediate between those of the pure components. In type II the boiling-point curves exhibit a maximum and in type III a minimum. The three types are illustrated in Figs. 20, 21 and 22.

Since the more volatile component is present in relatively greater proportion in the vapor phase than in the liquid phase, it will be evident that in the boiling-point-composition diagrams the upper curve always refers to the composition of the vapor phase. Thus we shall suppose that in Fig. 20, A represents water

and B methyl alcohol. A study of the diagram, as well as of the equations (67) and (68) of Chap. XI, enables us to determine what changes occur on isobaric distillation. If we start with a liquid whose composition is l, the vapor formed will have the composition v. The liquid will therefore become poorer in methyl alcohol and as the composition changes to l', the boiling-point will rise. If all the vapor formed be kept in contact with the liquid, evidently when the last drop of liquid is distilled, the vapor will have the composition v'', identical with l. If, however, (and this is of course the ordinary procedure) the vapor is removed by condensation, the boiling-point will rise until the last drop of liquid is pure water. By fractional distillation, any mixture can be more or less completely separated into the two components A and B. For if we were to redistil the fraction obtained as the composition of the liquid went from l to l', the fraction would have a composition intermediate between v and v' and on distilling would give at first a vapor richer in B than v.

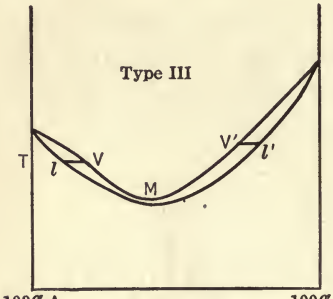


FIG. 22

Type II can be illustrated by mixtures of water and formic acid. A certain mixture of composition M has the maximum boiling-point for a given pressure. In this case it will be convenient to think of all mixtures to the left of M as consisting of the two components A and M, whereas for all mixtures to the right of M, the two components will be M and B. In the first case, A is the more volatile component, M the less volatile; in the second case, B is the more volatile and M the less volatile. Hence any mixture whose composition lies between pure A and M behaves like a mixture of type I and can be separated by fractional distillation into the two components A and M; similarly, for mixtures of M and B. On distillation of any mixture, then, the boiling-point will rise and if the vapor is removed the composition of the liquid will ultimately be that of M and the

liquid will distil at constant temperature since the composition remains invariable. This is a stable constant boiling-point, for if through any cause the composition of the liquid goes to the right or left of *M*, it will necessarily return to *M*. The constant boiling mixture behaves in some respects like a pure substance since it distils at constant temperature and pressure without change in composition. If however the pressure, at which the distillation is carried out, is altered, the composition of *M* is also altered and hence *M* corresponds to a mixture and not a pure substance. Other mixtures belonging to type II are the following: water and any one of the following acids: formic, hydrochloric, hydrobromic, hydriodic, hydrofluoric, nitric and perchloric; chloroform and acetone; chloroform and methyl acetate. In the case of water and some of the acids (e.g., HCl) we cannot at atmospheric pressure have liquids consisting of the two components in all imaginable proportions. If, in Fig. 21, *A* represents water and *B* represents HCl, the curves can be drawn only a certain distance to the right of *M*, ending at points corresponding to the most concentrated aqueous solution of the hydrogen chloride which has a total vapor pressure of one atmosphere. The following table contains some data with reference to mixtures having a maximum boiling-point. The data refer to atmospheric pressure.

TABLE X

Components	Maximum boiling-point	Composition of mixture of constant boiling-point
Water + HNO_3	120.5	68% HNO_3
Water + HCl	108.5	20.24% HCl
Water + HBr	126.0	47.5% HBr
Water + HI	127.0	57.0% HI
Water + HF	120.0	37.0% HF
Water + formic acid	107.1	77.0% formic acid
$CHCl_3$ + acetone	64.7	80.0% chloroform

In the case of water and HCl, the composition of the constant boiling mixture at different pressures is as follows: *

mm.	% HCl	mm.	% HCl
770	20.218	740	20.290
760	20.242	730	20.314
750	20.266		

* Roscoe and Ditmar, J. Chem. Soc., **12**, 128 (1860). Hulett and Bonner, J. Amer. Chem. Soc., **31**, 390 (1909).

A large number of pairs of liquids have boiling-point curves belonging to type III. We may mention the following: water and any one of ethyl alcohol, normal propyl alcohol, isopropyl alcohol, butyric acid and pyridine; benzene and any one of methyl, ethyl, allyl and tertiary butyl alcohols; acetone and carbon disulphide; ethyl alcohol and hexane, etc. In this case also it is convenient to think of any particular liquid mixture as consisting of the mixture with the minimum boiling-point and suitable amounts of either pure A or pure B. To any mixture whose composition as represented in Fig. 22 lies between that of A and M, we can apply the results deduced for type I mixtures. Thus by fractional distillation any such mixture can be more or less completely separated into A and M. Similarly for a mixture whose composition is between that of M and B, fractional distillation will effect a separation into M and B. But pure B cannot be obtained by distillation from a mixture whose composition is between that of M and A. If we start with a mixture whose composition differs by even a small amount from that of M, on continued distillation the composition of the liquid will depart more and more from that of M. This is clear from a study of Fig. 22. Since then the composition corresponding to M cannot in practice be reproduced with absolutely no error, it is impossible to make up mixtures of type III which will boil at a constant temperature for a considerable time; for the composition will gradually change and the temperature will gradually rise.

In the case of water (b.-p. = 100° C.) and ethyl alcohol (b.-p. = 78.3° C.) at atmospheric pressure, the minimum boiling-point is 78.13° C. for a mixture which is 95.57 per cent* alcohol by weight. The minimum boiling-point is thus very slightly below that of pure alcohol and the minimum point is very close to the alcohol axis. Any mixture containing less than 95.57 per cent of alcohol behaves like mixtures of type I and can be separated by fractional distillation into water and 95.57 per cent alcohol. In the case of any mixture which contains between 95.57 and 100 per cent alcohol, we shall in practice have a mixture which will boil at a fairly constant temperature since the maximum change in tem-

* Young and Fortey, Trans. Chem. Soc., **81**, 717 (1902).

perature is from 78.13° to 78.3°. Changes in composition will occur very slowly. Theoretically, it should be possible by fractional distillation to separate a 98 per cent alcohol into the two components, 95.57 per cent and 100 per cent; practically, however, the changes in composition on distillation would be so slight that the separation could not be effected without an excessively large number of distillations. For the rapidity of separation by fractional distillation depends to a large extent on the magnitude of the difference between the composition of the vapor and of the liquid from which the vapor has come. This difference is measured by the horizontal distance between the points on the two boiling-point curves in the figures. The farther apart the two curves are, the easier it will be to effect a separation of the components. In the case of water and ethyl alcohol, the two curves going from M (t = 78.13° C., composition = 95.57 per cent alcohol) to the point representing the boiling-point (78.3° C.) of pure alcohol, must be exceedingly close to each other.

Boiling-Points of Partially Miscible Liquids

If two liquids are soluble in each other in limited proportions, we shall have to consider the possibility of having two liquid phases in addition to the vapor phase. Since in accordance with the phase rule for a system of two components, $F = 4 - P$, we shall have two degrees of freedom, if we have a vapor phase and one liquid phase and one degree of freedom if we have a vapor phase and two liquid phases. If we make the pressure constant and equal to, say, one atmosphere, we shall have for two phases, one degree of freedom and for three phases, no degrees of freedom. For two phases, the boiling-point is a function of the composition of the phases; if three phases are present and the pressure is fixed, then the boiling-point and the composition of the phases are fixed. The boiling-point diagram for a system consisting of amyl alcohol and water at atmospheric pressure will be approximately that given in Fig. 23.

According to unpublished experiments of the author, the boiling-point at atmospheric pressure when the two liquid phases (each consisting of water and amyl alcohol) are present, is about

95° C. and the composition of the vapor phase is approximately 50 per cent by weight of either component. If we distil a homogeneous liquid of composition *l*, the vapor coming off will have the composition *v* and the temperature will rise gradually until the boiling-point of pure amyl alcohol is reached. If we start with a homogeneous liquid having the composition *l'*, the boiling-point will gradually rise until that of pure water is reached. If, however, we take quantities of amyl alcohol and water corresponding to a composition between *C* and *D*, the mixture will separate into two homogeneous liquid phases which will boil at the constant temperature of 95° C. At this temperature the composition of the phases is represented by the points *C* and *D* and on distillation the vapor from each phase has the composition *E*, where *E* is the point where the two vapor curves, *AE* and *BE*, meet. On continued distillation, one of the liquid phases will disappear. If the average composition of the two liquid phases was represented originally by a point to the left of *E*, then the phase of composition *D* will disappear and the boiling-point will rise as the composition moves along the curve *CA*. On the other hand, if the original heterogeneous mixture was richer in water than is represented by point *E*, the phase *C* will in time disappear and then the temperature will rise along the curve *DB*.

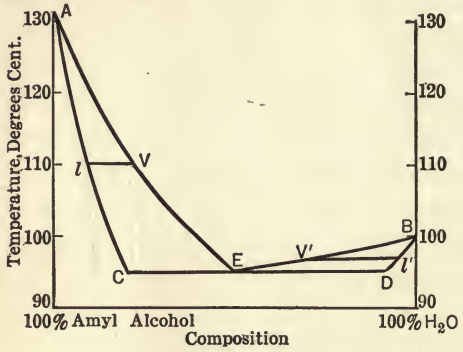


FIG. 23

Mixtures of methyl alcohol (b.-p. 64.7° C.) and carbon disulphide (b.-p. 46.3° C.) behave similarly to mixtures of amyl alcohol and water. The boiling-point when two liquid phases are present is about 38° C. and the vapor phase in these circumstances contains approximately 90 per cent by weight of carbon disulphide.

In the cases just considered, the boiling-point, when two liquid

phases were present, was lower than that of either component. It is possible however for the boiling-point when two liquid phases are present to be intermediate between those of the two components. This case is represented in Fig. 24, and is illustrated by mixtures of water and liquid SO_2. In the figure, C and D represent the composition of the two coexisting liquid phases with a constant boiling-point.

No matter what is the composition of the original mixture, the boiling-point will ultimately be that of pure A. Thus if we start with a homogeneous liquid corresponding to l, the boiling-point will rise until the liquid has the composition D. On continued heating the boiling-point will remain constant, and, since the vapor given off has the composition E, the other liquid phase represented by C will be simultaneously formed. Finally phase D will disappear and the boiling-point will follow the curve CA.

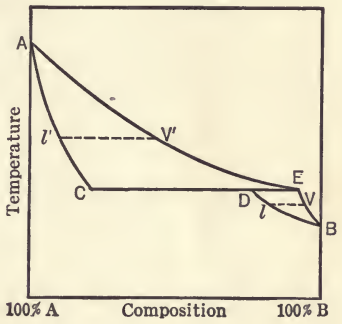


FIG. 24

The two cases just considered (represented in Figs. 23 and 24) are analogous to types I and III (Figs. 20 and 22). A third type in which the boiling-point of two liquid phases of two components would be higher than that of either pure component (analogous to type II, Fig. 21) does not appear to be possible. For assuming that two coexisting liquid phases containing two components have a boiling-point higher than either pure component, on distillation one of the phases must in general disappear. The boiling-point of the remaining single phase must now necessarily rise, which contradicts our hypothesis.

Two Immiscible Liquids

When two liquids are completely immiscible, the boiling-point diagram will always have the form illustrated in Fig. 25 in which AE, EB give the composition of the vapor and AC, CD, DB represent the composition of the liquid. In other words, the com-

position of the liquid phases will always be given by the points C and D, any point between C and D corresponding to a heterogeneous mixture of the two components. The boiling-point of the two liquid phases will be constant for a given pressure and it is easily shown that this boiling-point must be lower than that of either pure component. Since in practice no two liquids are absolutely insoluble in each other, Fig. 25 should be looked on as the limiting case of Fig. 23, when the points C and D approach infinitely close to the ordinates representing pure A and pure B. A full interpretation of Fig. 25 can be easily made when it is considered from this point of view. The composition E of the vapor from two immiscible liquids can be readily calculated. If at the boiling-point when the two liquid phases are present, the vapor pressures of the two pure liquids are p_A and p_B respectively, then in the vapor phase we have the relationship $\frac{p_A}{p_B} = \frac{n_A}{n_B}$ where n_A and n_B are the number of moles of A and B in a given amount of vapor. If m_A and m_B represent the actual weights of the two liquids in a given amount of vapor and if M_A and M_B are their respective molecular weights, then we have,

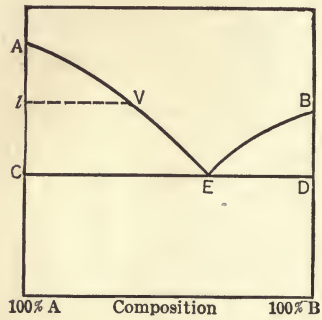


Fig. 25

$$n_A = \frac{m_A}{M_A}, \qquad n_B = \frac{m_B}{M_B}, \qquad \frac{m_A}{m_B} = \left(\frac{p_A}{p_B}\right)\frac{M_A}{M_B}.$$

If the molecular weight of B is much smaller than that of A, the proportion of A to B in the distillate will be much greater than the ratio of the corresponding vapor pressures of the two liquids. This fact is utilized in the distillation with steam of liquids immiscible with water and of high boiling-points and correspondingly low vapor pressures.

Liquid Phases in Absence of Vapor Phase

We shall now consider briefly the equilibrium between two liquid phases of two components at constant pressure, the pressure being sufficiently great to prevent the appearance of a vapor phase. Since we have already seen that the effect of pressure on a system in equilibrium depends on the magnitude of the volume changes produced when the pressure is altered and since these volume changes are very slight when the vapor phase is absent, we can infer that when we are dealing with liquid and solid phases only, we may ordinarily neglect the effect of pressure. Systems from which the vapor phase is absent we shall call condensed systems. If, then, in a condensed system, we assume that the pressure is constant, the number of degrees of freedom still at our disposal will be $N + 1 - P$ and for a condensed system of two components this becomes $3 - P$. If we consider the temperature and the composition of the phases as our variables, we see that if we have but one phase, there are two independent variables, whereas, if two phases exist, we have only one independent variable. Let us consider the equilibrium between two phases of the two components, water and aniline, at a pressure sufficient to prevent the appearance of a vapor phase. Fig. 26 will serve to describe this system.

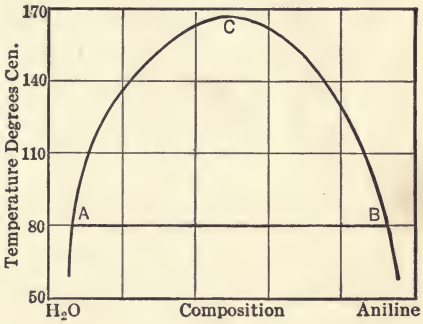


FIG. 26

Starting with pure water at 80° C., if we add a small quantity of aniline we shall obtain a homogeneous solution. On further addition of aniline the point A will be reached, representing an aqueous solution saturated with aniline. If more aniline is added, so that the whole mixture corresponds to a composition D, we shall have two layers, corresponding respectively to the points A and B. Since the system of two phases at constant pressure is a univariant system, on changing the temperature

the composition of each liquid will change in a perfectly definite manner as represented by the curves AC and BC. Above the curve ACB, we have the region of homogeneous solutions (one phase and therefore two degrees of freedom) so that both the temperature and the composition may be altered independently. In the diagram, the liquid phases are seen to approach each other in composition as the temperature is raised and at a temperature of 167° C. the two liquid phases become identical, with a composition of 48.6 per cent aniline. The point C is called the critical solution point. In some cases, liquids which are only partly miscible in each other at certain temperatures become completely miscible at lower temperatures. Such liquids are said to have an inferior critical solution temperature. This is the case with water and diethylamine, the inferior critical temperature being 143.5° C. It is to be noted that in all cases the critical solution temperature depends on the pressure. Some examples of liquids are known which possess both a lower and an upper critical temperature. This is the case with nicotine and water.

In many cases, there is a relationship between the concentrations of the two liquid phases which recalls the law of Cailletet and Matthias (equation (52), Chap. X). Thus if p_1 and p_2 are the percentages by weight of phenol in the two layers obtained from phenol and water, then $p_1 + p_2$ is a linear function of the temperature.

Some Applications of the Duhem-Margules Equation

The experimental study of the vapor pressures, total and partial, of liquid mixtures has shown that in many cases the vapor pressures can be expressed as rather simple functions of the composition. We shall consider examples of pairs of liquids miscible in all proportions so that the mole fractions, x_1 and x_2, may assume any value between 0 and 1. Let us investigate in the first instance the case in which the partial pressure p_1 of component 1 is proportional, at constant temperature, to its mole fraction x_1 in the liquid mixture; in other words

$$p_1 = P_1 x_1 . \qquad (1)$$

Evidently P_1 is the vapor pressure of the pure component 1, since $p_1 = P_1$ when $x_1 = 1$. From equation (1), we find $x_1 \frac{d \log p_1}{dx_1} = 1$. Hence according to the Duhem-Margules equation (equation (66), Chap. XI), $x_2 \frac{d \log p_2}{dx_2} = 1$, and therefore

By integration . . $p_2 = P_2 x_2 = P_2 (1 - x_1)$, (2)

where P_2 is the integration constant. P_2 is evidently the vapor pressure of the second component in the pure state. The total vapor pressure $p = p_1 + p_2$ is given by the equation

$$p = P_1 x_1 + P_2 (1 - x_1). \tag{3}$$

Hence if either partial vapor pressure is a linear function of x_1 or x_2, the same is true of the total vapor pressure. If the pressures are plotted in diagrams as in Figs. 17, 18 and 19, the curves referring to the pressures as functions of the composition of the liquid will be straight lines. If, however, we plot the curves as functions of the composition of the vapor phase, we shall have quite different results. For if y_1 and y_2 are the mole fractions in the vapor phase,

$$y_1 = \frac{p_1}{p} = \frac{P_1 x_1}{P_1 x_1 + P_2 (1 - x_1)}, \tag{4}$$

and

$$x_1 = \frac{P_2 y_1}{P_1 + (P_2 - P_1) y_1}.$$

Hence we can obtain

$$p_1 = \frac{P_1 P_2 y_1}{P_1 + (P_2 - P_1) y_1}; \qquad p_2 = \frac{P_1 P_2 (1 - y_1)}{P_1 + (P_2 - P_1) y_1};$$

$$p = \frac{P_1 P_2}{P_1 + (P_2 - P_1) y_1}. \tag{5}$$

Thus the vapor pressure curves as functions of y_1 are no longer straight lines. If, for the sake of brevity, we call the vapor pressure curves plotted against the composition of the liquid, the x-curves, and those plotted against the composition of the vapor, the y-curves, it is easy to show that the y-curve is always below the corresponding x-curve as illustrated in Fig. 17. It is also

easy to show that the y-curves have no maximum or minimum point. From equations (1) and (2), we also have, since $\frac{p_2}{p_1} = \frac{y_2}{y_1}$,

$$\frac{y_2}{y_1} = \frac{P_2}{P_1}\left(\frac{x_2}{x_1}\right). \tag{6}$$

According to (6), the ratio of the two components in the vapor phase is proportional to the ratio in the liquid phase, the proportionality factor being given by the ratio of the vapor pressures of the two components in the pure state.

The behavior just discussed and summarized in equations (1) to (6) is exhibited by a number of pairs of liquids, usually by pairs of closely related liquids. We may mention as examples: chlorobenzene and bromobenzene; ethyl propionate and ethyl acetate; ethyl benzene and toluene; *n*-octane and *n*-hexane; toluene and benzene; ethylene dichloride and propylene dibromide, etc.

In other cases equation (1) does not hold but must be replaced by the following:

$$p_1 = P_1 x_1^{\,a}. \tag{7}$$

Employing the Duhem-Margules relation, we find that if equation (7) is valid, then we must have

$$p_2 = P_2 x_2^{\,a} = P_2 (1 - x_1)^a. \tag{8}$$

Hence the total vapor pressure p is

$$p = p_1 + p_2 = P_1 x_1^{\,a} + P_2 (1 - x_1)^a \tag{9}$$

and the vapor pressure curves are no longer linear functions of x_1 or x_2. We also have instead of equation (6)

$$\frac{p_2}{p_1} = \frac{y_2}{y_1} = \frac{P_2}{P_1}\left(\frac{x_2}{x_1}\right)^a. \tag{10}$$

From equation (9), we obtain, on differentiation,

$$\frac{dp}{dx_1} = a\left[P_1 x_1^{\,a-1} - P_2 (1 - x_1)^{a-1}\right] \tag{11}$$

$$\frac{d^2p}{dx_1^{\,2}} = a\,(a - 1)\left[P_1 x_1^{\,a-2} + P_2 (1 - x_1)^{a-2}\right].$$

The x-curve of total vapor pressure will have an extreme value when $\frac{dp}{dx} = 0$, or when

$$1 = \frac{P_2}{P_1}\left(\frac{x_2}{x_1}\right)^{a-1} \quad \text{or} \quad \frac{x_2}{x_1} = \frac{P_2}{P_1}\left(\frac{x_2}{x_1}\right)^{a}. \tag{12}$$

But from equation (10), we see that at the extreme point $\frac{y_2}{y_1} = \frac{x_2}{x_1}$, or the vapor and the liquid have the same composition. Whether the extreme point is a maximum or minimum depends on the sign of $\frac{d^2p}{dx_1^2}$ when $\frac{dp}{dx_1}$ is zero and therefore on the sign of the quantity $a\,(a-1)$. Now a is always positive. Hence when a is greater than unity, the x-curve of total vapor pressure will have a minimum point; when a is between 0 and 1, the curve will exhibit a maximum. Finally if $a = 1$, the x-curve is a straight line and therefore of course has no maximum or minimum point. Ethyl alcohol and ethyl ether are a pair of liquids for which equation (7) is valid, the value of a at 7.2° C. being 0.5. Hence the vapor pressure curve for mixtures of these two liquids has a maximum point.

There are many pairs of liquids for which even equation (7) is not valid, much more complicated equations being required to express the vapor pressures as functions of the composition. We shall however omit a consideration of these more complex cases.

. . . . . .

If a system of two components in two phases is in thermodynamic equilibrium, certain relations between the variables of the system must be satisfied. These relations were given in Chap. XI in a variety of forms (see equations (51) and (53), (56) and (57), (62), (63), (64)). In equations (62), (63), and (64) of Chap. XI, one of the phases is supposed to be an ideal gas-mixture. Some of these equations contain the quantities B' and B'' defined by equations (55). By assuming the vapor phase to consist of ideal gases, we found it possible to express B'' in a very simple way in terms of the variables T, p and p_1 (see equation (61) of Chap. XI). By means of equations (65) of Chap. XI,

we can express B' explicitly in terms of T, p and p_1 if p_1 is a known function of x_1; for such mixtures the value of B' can be easily calculated and inserted in the equations (62), (63) and (64).

Let us assume then that we have a mixture of two liquids, the vapor pressures of which are given by equations (7), (8) and (9) of this chapter. By putting a equal to unity, we also include the case in which the vapor pressures are linear functions of x_1. Since then $p_1 = P_1 x_1^a$, and therefore $x_1 \left(\frac{d \log p_1}{dx_1}\right) = a$ or $d \log p_1 = a\, d \log x_1$, the value of B' is, from equation (65) of Chap. XI,

$$B' = a x_1 RT = \frac{N_1}{N_1 + N_2} a\, RT. \tag{13}$$

For liquid mixtures in which p_1 is a linear function of x_1, B' would equal $x_1 RT = \frac{N_1}{N_1 + N_2} RT$. Substituting the value of B' from equation (13) in equations (64) of Chap. XI, we may write

$$\left.\begin{aligned} -L_1\, d \log T + RT\, d \log p_1 - aRT\, d \log x_1 &= 0, \\ -L_2\, d \log T + RT\, d \log p_2 - aRT\, d \log x_2 &= 0. \end{aligned}\right\} \tag{14}$$

If the temperature is maintained constant, evaporation or distillation will proceed subject to the condition

$$d \log \left(\frac{p_2}{p_1}\right) = a\, d \log \left(\frac{x_2}{x_1}\right), (T = \text{constant}). \tag{15}$$

Since a is positive, we see that as distillation proceeds the composition of both phases changes in the same sense. Multiplying the first equation of (14) by p_1 and the second by p_2 and adding, we obtain

$$-(p_1 L_1 + p_2 L_2)\, d \log T + RT\, dp - aRT\, (p_1\, d \log x_1 + p_2\, d \log x_2) = 0.$$

And since

$$d \log x_2 = \frac{dx_2}{x_2} = -\frac{dx_1}{x_2} = -\frac{x_1}{x_2} d \log x_1,$$

the equation becomes

$$-(p_1 L_1 + p_2 L_2)\, d \log T + RT\, dp + \frac{a\, p_1 x_1}{x_2} \left(\frac{p_2}{p_1} - \frac{x_2}{x_1}\right) RT\, d \log x_1 = 0. \tag{16}$$

If the distillation is carried out at constant pressure, $dp = 0$ and we have

$$d \log x_1 = \frac{x_2 (p_1 L_1 + p_2 L_2)}{a x_1 p_1 \left(\frac{p_2}{p_1} - \frac{x_2}{x_1} \right) RT^2} dT. \tag{17}$$

If the second component is the more volatile one, it is present in the vapor phase in greater proportion than in the liquid phase; that is $\frac{p_2}{p_1}$ is greater than $\frac{x_2}{x_1}$. As the distillation proceeds at constant pressure, dT is positive and hence $d \log x_1$ is positive or the mole fraction of the less volatile component in the liquid increases. If finally the partial vapor pressure p_2 of the second component is maintained constant, $dp_2 = 0$ and hence we can deduce from the equations (14) the following relations:

$$\left.\begin{aligned} d \log p_1 &= \frac{\left(L_1 + \frac{x_2}{x_1} L_2 \right)}{RT^2} dT \\ d \log x_2 &= -\frac{L_2}{aRT^2} dT \end{aligned}\right\} \quad p_2 = \text{constant.} \tag{18}$$

We can interpret equations (18) in the following manner: If the temperature of the system we have under consideration is raised and if at the same time the partial vapor pressure of the second component is maintained constant, the increase in the partial vapor pressure of the first component is given by the first equation of (18). At the same time the concentration of the second component in the liquid will decrease, the magnitude of the change being given by the second equation of (18). If V_m liters is the volume of the liquid containing x_1 moles of the first component and x_2 moles of the second, then the concentration C_2 of the second component in the liquid is $C_2 = \frac{x_2}{V_m}$. If we assume that V_m is practically independent of x_2 and T (which will be the case if x_2 is small) then $d \log x_2 = d \log C_2$ and we have

$$d \log C_2 = -\frac{L_2}{aRT^2} dT, \tag{19}$$

which may be interpreted as showing how the solubility of a gas at constant partial pressure varies with the temperature. If x_2 is exceedingly small, the first equation of (18) becomes $d \log p_1 = \frac{L_1}{RT^2} dT$, which is one of the approximate forms of the Clapeyron-Clausius formula.

PROBLEMS

1. Using Fig. 15, compare the densities of Ice I, Ice III, Ice V and Ice VI with that of liquid water.

2. Compare the densities of rhombic, monoclinic and liquid sulphur. (See Fig. 16.)

3. The per cent by weight of phenol in the two liquid phases of the two components phenol and water is as follows: 45° C., 10.62 and 65.02; 55° C., 13.88 and 60.18; 65° C., 22.26 and 49.34. Calculate the composition of each phase at 68.8° (the critical solution temperature).

4. Water and C_6H_5Cl are practically immiscible. Their vapor pressures are at 90° C., 525.45 and 208.35 mm.; at 91° C., 545.8 and 215.8 mm. Calculate the boiling point of a mixture of water and C_6H_5Cl under a pressure of 740.2 mm. and also the composition of the distillate, assuming the vapors to be ideal gases.

5. A mixture of C_6H_5Cl and C_6H_5Br obeys the linear formula (equation (1)). At 136.7° C., the vapor pressure of C_6H_5Cl is 863 mm. (P_1) and of C_6H_5Br is 453 mm. (P_2). (*a*) What mixture has a total vapor pressure of 760 mm.? (*b*) What is the molecular ratio of chlorobenzene to bromobenzene in the vapor from mixtures containing one per cent of C_6H_5Cl? one per cent of C_6H_5Br? (*c*) What is the composition of the liquid when the partial pressures of the two components are equal?

6. Benzene and ethylene dichloride obey equation (1). At a certain temperature $P_1(C_6H_6) = 268.0$ mm. and $P_2(C_2H_4Cl_2) = 236.2$ mm. What is the molecular composition y_1 of the vapor when $x_1 = 0.5$? What is the value of x_1 when $y_1 = 0.5$?

7. What is the physical significance of equations (7), (8) and (9) when a is zero?

8. Assume that ethyl alcohol and ether follow equation (7). At 7.2° C., the vapor pressures are $P_1 = 24.37$ and $P_2 = 264.7$ mm., and $a = 0.5$. What are the total vapor pressures of mixtures containing $\frac{1}{2}$, $\frac{1}{3}$ and $\frac{1}{5}$ of their weights of alcohol and what is the composition of the mixture of maximum vapor pressure?

9. For the range of temperatures 48°–77°, we have the equation $\frac{1 - y_1}{y_1} = 3.32 \left(\frac{1 - x_1}{x_1}\right)^{0.9}$ where x_1 is the mole fraction of benzene in a

mixture of benzene and carbon disulphide. Find the per cent by weight of C_6H_6 in the distillate from mixtures containing 95, 50 and 20 per cent by weight of benzene. Find also the ratio of the vapor pressures of the pure liquids.

CHAPTER XIII

APPLICATIONS OF THE PHASE RULE II

Dilute Solutions

In Chap. XI (equation (66)) we found that the change in the partial vapor pressures of a solution of two components due to a change in the composition is given by the Duhem-Margules formula. But in order to apply the formula to finite changes in the composition, it is necessary to obtain it in an integral form and this requires a knowledge of one of the partial vapor pressures as a function of the composition. Now the partial vapor pressures are in most cases rather complicated functions of the mole fractions and these functions must ordinarily be determined by actual experiment. There is, however, a class of solutions for which a general law has been established and we shall use this law in determining some of their thermodynamic properties. We refer to that class of solutions in which one of the components is present in large excess, so that its mole fraction is but slightly less than unity. If we represent the composition of a solution of two components by the mole numbers, N_1 and N_2, or the mole fractions, x_1 and x_2, then we shall have a dilute solution when N_1 is much larger than N_2, or when x_1 is approximately unity. We shall refer to component one as the solvent. If $(p_1)_0$ is the vapor pressure of the pure solvent at the temperature T, and p_1 is its vapor pressure in the solution, we can express the relation between $(p_1)_0$, p_1 and x_1 by means of Raoult's Law. This law was established by Raoult on the basis of numerous experiments and has been confirmed by later investigators. We shall take it to be a fundamental law for dilute solutions. It may be expressed in the following forms:

$$\frac{(p_1)_0 - p_1}{(p_1)_0} = \frac{N_2}{N_1 + N_2} = x_2, \quad \frac{p_1}{(p_1)_0} = x_1 \quad \text{or} \quad p_1 = x_1(p_1)_0. \quad (1)$$

The vapor pressure of the solvent in a dilute solution is equal to the vapor pressure of the pure solvent multiplied by its mole fraction. Writing the Duhem-Margules equation in the form

$$x_1 \frac{d \log p_1}{dx_1} + x_2 \frac{d \log p_2}{dx_1} = 0, \tag{2}$$

we obtain, from equation (1), $x_1 \frac{d \log p_1}{dx_1} = 1$ and since $dx_2 = -dx_1$

$$p_2 = (p_2)_0 x_2 \tag{3}$$

where $(p_2)_0$ is a constant at a given temperature. Equations (1) and (3) are taken to be valid for dilute solutions only. $(p_2)_0$ is evidently the vapor pressure of pure component two. If Φ_1 is the thermodynamic potential of one mole of component one, we have, in general, for changes in temperature and pressure,

$$d\Phi_1 = -S_1 \, dT + V_1 \, dp_1. \tag{4}$$

Now the potentials of components in a liquid or solid phase are equal to the potentials of the components in the coexisting vapor phase. We can therefore find the difference between the potential of the pure solvent and the solvent in the solution by finding the difference in the potentials when the vapor of the solvent is at a pressure $(p_1)_0$ and when its pressure is p_1. Assuming the vapor to be an ideal gas, equation (4) may be written for isothermal changes,

$$d\Phi_1 = \frac{RT}{p_1} dp_1 = RT \, d \log p_1, (T = \text{constant}). \tag{5}$$

Hence if $(\Phi_1)_0$ is the thermodynamic potential of one mole of the pure solvent,

$$\Phi_1 = (\Phi_1)_0 + RT \log \frac{p_1}{(p_1)_0} = (\Phi_1)_0 + RT \log x_1. \tag{6}$$

In the same way, if $(\Phi_2)_0$ and Φ_2 are the thermodynamic potentials of one mole of component two in the pure state and in the solution, we find, from equation (3),

$$\Phi_2 = (\Phi_2)_0 + RT \log x_2. \tag{7}$$

If the solution contains N_1 and N_2 moles of components one and two, the total thermodynamic potential of the solution will be

$$\Phi = N_1(\Phi_1)_0 + N_2(\Phi_2)_0 + N_1 RT \log x_1 + N_2 RT \log x_2.$$

The foregoing results can be readily extended to a dilute solution of any number of components. Thus if x_1, x_2, x_3 . . . are the mole fractions and if component one is the solvent and hence x_1 is only slightly less than unity, the total thermodynamic potential of the solution will be

$$\Phi = N_1(\Phi_1)_0 + N_2(\Phi_2)_0 + N_3(\Phi_3)_0 + \cdots + RT(N_1 \log x_1 + N_2 \log x_2 + N_3 \log x_3 + \cdots). \quad (8)$$

In equation (76), Chap. XI, we have a criterion as to whether a solution can be considered as dilute. According to this equation the heat H_d evolved when one mole of solvent is added to an infinite amount of a solution of a given composition is

$$H_d = RT^2 \left(\frac{d \log \frac{p}{p_0}}{dT} \right)_r, \quad (9)$$

where $H_d = M_1 h_d$ and r is the ratio of the two components. If the second component (the solute) has a negligible vapor pressure, we can let p and p_0 refer to the solvent. Now, according to equation (1), $\frac{p}{p_0}$ is equal to x_1 and is constant if r is constant. Accordingly the heat of dilution of a dilute solution is zero.

Solutions Containing an Involatile Solute

If in a solution of two components, the solute has a negligible vapor pressure, the equations we have developed will still hold, but we can consider the vapor phase as consisting exclusively of the solvent. Thus we can write p_0 instead of $(p_1)_0$ and p instead of p_1 in equations (1), and we shall have $p = x_1 p_0$. Let us calculate the boiling-point of such a dilute solution. Let T_b be the boiling-point of the pure solvent at the pressure p_0 and let p_1 be the vapor pressure of the solution at this temperature. We have to calculate how much the temperature of the solution

must be raised in order that its vapor pressure may equal p_0. According to equation (75) Chap. XI, $\lambda_r - \lambda = h_d$, or, in terms of moles, $L_r - L = H_d$. Now for dilute solutions, H_d is zero. Accordingly instead of L_r we may write L. According to equation (74), Chap. XI,

$$\left(\frac{dT}{dp}\right)_r = \frac{RT^2}{Lp},$$

or

$$\frac{dT}{T^2} = \frac{R}{L} d \log p. \tag{10}$$

We can integrate this, assuming that over small intervals of temperature, L, the molar heat of vaporization, is constant. Since at the temperature T_b our solution has the vapor pressure, $p_1 = x_1 p_0$, we obtain on integration

$$\frac{T - T_b}{TT_b} = \frac{R}{L} \log \frac{p}{p_1}.$$

Therefore the temperature T at which the vapor pressure of the solution is equal to p_0, is given by the equation

$$T - T_b = \frac{RTT_b}{L} \log \frac{p_0}{p_1} = \frac{RTT_b}{L} \log \frac{1}{x_1}. \tag{10a}$$

Since the solution is supposed to be dilute, T does not differ much from T_b and since $x_1 = 1 - x_2$, we obtain, writing $\Delta T = T - T_b$,

$$\Delta T = -\frac{RT_b^2}{L} \log_e (1 - x_2). \tag{11}$$

Expanding the term $\log_e (1 - x_2)$ we obtain

$$\Delta T = \frac{RT_b^2}{L} \cdot \left(x_2 + \frac{x_2^2}{2} + \frac{x_2^3}{3} + \cdots\right). \tag{12}$$

And finally, since x_2 is very small,

$$\Delta T = x_2 \cdot \frac{RT_b^2}{L}, \tag{13}$$

which gives the relation between the boiling-point of the pure solvent and of a solution of an involatile solute whose molar fraction is x_2. It should be noted that when we introduced the

term $L = M_1\lambda$ (where λ is the heat of evaporation of one gram of the solvent), the molecular weight M_1 referred to the solvent in the gaseous state. The molecular elevation of the boiling-point is usually defined as the elevation produced by 1 mole of solute in 1000 grams of solvent. Thus if we have N_1 moles of solvent and N_2 moles of solute, $x_2 = \dfrac{N_2}{N_1 + N_2}$ and this is practically equal to $\dfrac{N_2}{N_1}$. But if $N_1 = \dfrac{1000}{M_1}$, $x_2 = \dfrac{N_2 M_1}{1000}$ and equation (13) becomes

$$\Delta T = \frac{N_2 M_1 R T_b^2}{1000\, L} = \frac{N_2 R T_b^2}{1000\, \lambda},$$

since

$$\lambda = \frac{L}{M_1}.$$

Therefore, the elevation for 1 mole of solute in 1000 grams of solvent is $\dfrac{\Delta T}{N_2}$ or

$$E = \frac{R T_b^2}{1000\, \lambda} = \frac{0.002\, T_b^2}{\lambda}, \qquad (14)$$

since $R = 1.987$ or practically 2. We give herewith the values of E for a number of solvents.

TABLE XI

Solvent	E
Water	0.52
Ether	2.12
Benzene	2.67
Chloroform	3.66
Aniline	3.22
Acetic acid	2.53

Freezing-Points of Dilute Solutions

For the sake of clearness we shall suppose that water is the solvent and we shall calculate the freezing-point of an aqueous solution. We shall assume that the phase which separates out on freezing is pure ice. Let p_i be the vapor pressure of ice, p_w

that of liquid water and p_s that of the solution, in which the mole fraction of water is x_1 and of the solute x_2. Let $(p_i)_0$, $(p_w)_0$ and $(p_s)_0$ be the values of the vapor pressure at the freezing-point T_f of pure water. Then $(p_i)_0 = (p_w)_0$ and at all temperatures $p_s = x_1 p_w$. The molar heat of fusion, L_f, will be essentially the same for the dilute solution as for pure water. We shall also suppose that L, the molar heat of vaporization, is a constant over the small temperature interval considered. Applying the Clausius-Clapeyron formula, we have

$$\frac{dp_i}{p_i} = \frac{L + L_f}{RT^2} dT$$

or on integration

$$\log_e \frac{p_i}{(p_i)_0} = \frac{T - T_f}{RTT_f} (L + L_f).$$

Similarly for the solution

$$\frac{dp_s}{p_s} = \frac{L}{RT^2} dT,$$

$$\log_e \frac{p_s}{(p_s)_0} = \log \frac{p_s}{x_1 (p_i)_0} = \frac{T - T_f}{RTT_f} L = \log \frac{p_s}{(p_i)_0} - \log x_1.$$

If T is the temperature at which ice and solution are in equilibrium, then at this temperature $p_i = p_s$ and hence

$$\frac{T - T_f}{RTT_f} (L + L_f) = \frac{T - T_f}{RTT_f} L + \log x_1.$$

Therefore we have, since $x_1 = 1 - x_2$,

$$-\Delta T_f = T_f - T = -\frac{RTT_f}{L_f} \log_e (1 - x_2). \qquad (15)$$

But, since x_2 is small, T is not very different from T_f, and we obtain finally

$$-\Delta T_f = \frac{x_2 RT_f^2}{L_f}. \qquad (16)$$

This equation for the lowering of the freezing-point is identical in form with equation (13) for the elevation of the boiling-point.

Hence if K is the lowering of the freezing-point produced by 1 mole of solute in 1000 grams of solvent, we obtain

$$K = \frac{RT_f^2}{1000\,\lambda_f} = \frac{0.002\,T_f^2}{\lambda_f}, \tag{17}$$

where λ_f is the latent heat of fusion of one gram of solvent. The following table gives the values of the molecular depression constant for a number of solvents.

TABLE XII

Solvent	K
Water	1.86
Acetic acid	3.88
Benzene	5.12
Phenol	7.4
Nitrobenzene	7.0

The usefulness of equations (14) and (17) in determining the molecular weights of dissolved substances in dilute solution will be obvious to the reader. Thus if m grams of an involatile substance are dissolved in 1000 grams of a solvent, for which the boiling-point and freezing-point constants are E and K, and if Δ represents either the elevation of the boiling-point or the lowering of the freezing-point, then the molecular weight M of the dissolved substance is

$$M = \frac{mE}{\Delta} \quad \text{or} \quad M = \frac{mK}{\Delta}. \tag{18}$$

Henry's Law

We shall now consider a type of dilute solution in which the solute is very volatile, so that although its mole fraction in the liquid phase is very small, its mole fraction in the vapor phase may approach unity. If we bring hydrogen and water together at ordinary temperatures, we shall have an example of the type we are now to study. Let p_1 and p_2 be the partial pressures of water vapor and hydrogen, and let x_1 and x_2 be the mole fractions in the liquid phase. Let p be the total vapor pressure and

p_0 be the vapor pressure of pure water. For this dilute solution, according to Raoult's law,

$$p_1 = x_1 p_0. \tag{19}$$

Applying the Duhem-Margules equation, $x_1 \frac{d \log p_1}{dx_1} - x_2 \frac{d \log p_2}{dx_2}$ $= 0$ (since $dx_1 = -dx_2$), we find that $x_2 \frac{d \log p_2}{dx_2} = 1$ and hence

$$p_2 = k' x_2 \quad \text{or} \quad x_2 = k p_2. \tag{20}$$

In words, the mole fraction of hydrogen in the solution is, at a given temperature, proportional to the partial pressure of the hydrogen. The assumptions explicitly or implicitly made in the deduction of equation (20) are: (1) the gases (water vapor and hydrogen) are ideal gases, (2) the aqueous solution is a dilute one, (3) the gas dissolves in the liquid without change in mole number of the gas. Equation (20) may be taken as a statement of Henry's Law in regard to the solubility of gases in liquids. Equation (20) will evidently hold most accurately when the solubility of the gas is not large and when the gas is approximately ideal. Henry's Law cannot be expected to hold if the mole number of the gas changes when it dissolves in the liquid and this will in general be the case if a chemical change takes place. Thus Henry's Law does not hold for the solubility of hydrogen chloride in water. We have evidence that in this case a chemical change occurs, for the absorption of hydrogen chloride in water is accompanied by a considerable heat effect and moreover the theory of ionization leads us to infer that in the aqueous solution the hydrogen chloride is dissociated to a large extent into ions.

Henry's Law may be expressed in terms of the concentrations of the gas in the two phases. Let v_1 be the specific volume of the solvent and therefore that of the dilute solution, and let M_1 be the molecular weight of the solvent. In one liter of the dilute solution there are therefore $\frac{1000}{M_1 v_1}$ moles of solvent and $\frac{1000}{M_1 v_1} \frac{x_2}{x_1}$ or practically $\frac{1000}{M_1 v_1} x_2$ moles of solute (since x_1 is almost unity). If

C_2 and c_2 are the concentrations in moles per liter of the gas in the liquid and gaseous phases, then

$$C_2 = \frac{1000}{M_1 v_1} x_2 \quad \text{and} \quad c_2 = \frac{p_2}{RT}.$$

According to equation (20), $x_2 = kp_2$; therefore,

$$C_2 = \left(\frac{1000}{M_1 v_1} kRT\right) c_2 = k' c_2, \tag{21}$$

where k' is a function of the temperature. Henry's Law, as given by equation (21), may be stated as follows: At a given temperature, a gas distributes itself between a gaseous and liquid phase so that the ratio of its concentrations in the two phases is a constant. The solubility of gases in liquids is usually given in terms of what is called the absorption-coefficient. The absorption-coefficient α of a gas in a liquid at $T°$ is defined as the volume of the gas (measured at 0° C. and 1 atmosphere) absorbed by unit volume of the liquid at $T°$ when the partial pressure, p_2, of the gas is one atmosphere. It is easy to show that the relation between the absorption-coefficient and the k' of equation (21) is given by the equation

$$\alpha = \frac{273}{T} k'. \tag{22}$$

Thus equation (21) may be expressed as follows in terms of the absorption-coefficient:

$$C_2 = \frac{T}{273} \alpha c_2 = \frac{\alpha p_2}{273 R}, \tag{23}$$

where α is a function of the temperature.

Equations (20), (21) or (23) enable us to determine the solubility of a gas in a solvent under different partial pressures p_2. The solubility will however change with the temperature, and the law governing this is given in equation (19), Chap. XII, in which we set a equal to 1 (since we have a linear law for the relation between the partial pressures and the composition of the liquid). Thus we have

$$d \log C_2 = -\frac{L_2}{RT^2} dT, \ (p_2 = \text{constant}), \tag{24}$$

where L_2 is the heat absorbed when one mole of the gas is evaporated from a large amount of the solution at the temperature T. If we assume L_2 to be a constant and if $(C_2)_2$ and $(C_2)_1$ are the concentrations of the gas in the liquid at the temperatures T_2 and T_1, we obtain on integrating (24)

$$\log_e \frac{(C_2)_2}{(C_1)_1} = -\frac{L_2 (T_2 - T_1)}{RT_1T_2}, \ (p_2 = \text{constant}). \qquad (25)$$

If, as is in general the case, L_2 is positive, we see that the solubility of the gas diminishes as the temperature increases. From equation (23), $d \log C_2 = d \log \alpha$ when p_2 is constant. Hence if α_1 and α_2 are the absorption-coefficients at the temperatures T_1 and T_2,

$$\log_e \frac{\alpha_2}{\alpha_1} = -\frac{L_2 (T_2 - T_1)}{RT_1T_2}, \ (p_2 = \text{constant}). \qquad (26)$$

The absorption-coefficient of a gas which follows Henry's Law decreases in general as the temperature is raised.

Osmotic Pressure of Dilute Solutions

In a system which is in thermodynamic equilibrium, the potential of each component is the same in all phases if each component can pass without hindrance from any one phase to any other phase (see equations (10) of Chap. XI). But if conditions are such that a certain component cannot pass from one phase to another, the potentials of this component may be different in the different phases. For the sake of clearness, let us suppose that we have a system consisting of pure water, an aqueous solution of cane sugar and water vapor. Let the vessel in which the system is confined be so constructed that the water and the sugar solution are separated by a membrane permeable only to the water. When thermodynamic equilibrium is reached, the potential of the water must be the same at the boundary of all the phases. As is well known from the experiments of Pfeffer and others, water will go from the pure solvent into the solution and if the external pressure at the surfaces of the two liquids is equal, the level of the solution will rise until the pressure due to the height of the column of solution above the level of the pure solvent pre-

vents further osmosis. Instead of allowing equilibrium to be reached in this manner, the transfer of water across the semi-permeable membrane can be prevented by increasing the external pressure on the solution. If P_1 is the pressure on the pure solvent, and P_2 is the pressure on the solution, the osmotic pressure, P, of the solution is defined as equal to $P = P_2 - P_1$, when these pressures are sufficient to maintain the solvent and solution in thermodynamic equilibrium. Under these circumstances, the vapor pressure of the solution under a pressure P_2 must equal that of the pure water under the pressure P_1. By means of equation (32) or (34), Chap. X, we can determine the relation between P_1, P_2 and the vapor pressures of solvent and solution. Let p_0 and p_1 be the vapor pressures of pure water and of solution under the pressure P_1 which we shall take to be constant and equal to p_0. (Since the vapor pressures of liquids change only slightly with change in pressure we might even consider P_1 as constant and equal to one atmosphere.) Substituting in equation (34), Chap. X, we have

$$\left.\begin{aligned} \log_e \frac{p_0}{p_1} = \frac{M_1 v_1}{RT}(P_2 - P_1) &= M_1 \frac{P v_1}{RT}, \\ P &= -\frac{RT}{M_1 v_1} \log_e \frac{p_1}{p_0}. \end{aligned}\right\} \qquad (27)$$

In equation (27), M_1 is the molecular weight of the solvent as a gas and v_1 is the increase in the volume of a large amount of the solution when one gram of the solvent is added to it. In the case of dilute solutions, v_1 is practically the specific volume of the solvent. The assumptions made in deducing (27) are: (1) the vapor of the solvent is an ideal gas, (2) the specific volume of the solution is negligible in comparison with that of the vapor, (3) the solution is practically incompressible. On the basis of these assumptions equation (27) is valid for a solution of any concentration. For dilute solutions, it can be put into simpler forms. Thus if x_1 is the mole fraction of the solvent and x_2 that of the solute, we have, from equation (19) for dilute solutions, $\frac{p_1}{p_0} = x_1$ and hence

$$P = -\frac{RT}{M_1 v_1} \log_e x_1 = -\frac{RT}{M_1 v_1} \log_e (1 - x_2). \qquad (28)$$

Since $$-\log_e (1 - x_2) = x_2 + \frac{x_2^2}{2} + \frac{x_3^2}{3} + \ldots,$$

we have, when x_2 is small,

$$P = \frac{x_2 RT}{M_1 v_1}. \tag{29}$$

Now in the case of dilute solutions, $M_1 v_1$ is practically the volume of the solution which contains one mole of solvent. If the solution consists of N_1 moles of solvent and N_2 moles of solute, $x_2 = \frac{N_2}{N_1 + N_2}$ and therefore approximately $x_2 = \frac{N_2}{N_1}$. If we represent by V the total volume of the solution, V is equal to $N_1 M_1 v_1$ and hence from (29)

$$PV = N_2 RT, \tag{30}$$

valid only for very dilute solutions.

Returning to a consideration of equation (27) let s be the density of a solution containing N_1 moles of solvent and N_2 moles of solute and let V liters be the volume of this amount of solution. Let $c = \frac{N_2}{V}$ be the molar concentration of the solute. Then $1000\, sV = N_1 M_1 + N_2 M_2$. The expression $M_1 v_1$ in equation (27) is equal to $\left(\frac{dV}{dN_1}\right)_{N_2}$. Hence

$$\frac{1}{M_1 v_1} = \left(\frac{dN_1}{dV}\right)_{N_2} = \frac{1000}{M_1}\left[s + V\left(\frac{ds}{dV}\right)_{N_2}\right]. \tag{31}$$

But since $$c = \frac{N_2}{V},$$

$$dV = -\frac{N_2}{c^2}\, dc = -\frac{V}{c}\, dc.$$

Hence equation (31) may be written

$$\frac{1}{M_1 v_1} = \frac{1000}{M_1}\left(s - c\frac{ds}{dc}\right), \tag{32}$$

and therefore equation (27) becomes

$$P = -\frac{1000\, RT}{M_1}\left(s - c\frac{ds}{dc}\right)\log_e \frac{p_1}{p_0}. \tag{33}$$

In very dilute solutions, $c = 0$ and $s = s_0$, the density of the pure solvent, and

$$P = -\frac{1000\, s_0}{M_1} RT \log_e \frac{p_1}{p_0}. \qquad (34)$$

In general, however, in concentrated solutions, the variation of the density of the solution with the concentration must be known before the osmotic pressure can be calculated from p_1 and p_0. But even in concentrated solutions, if the density is a linear function of the concentration, that is, if $s = s_0 + kc$, then $s - c\frac{ds}{dc} = s_0$ and equation (34) is valid. Since the relation $s = s_0 + kc$ frequently holds, we can expect equation (34) to be approximately valid even for concentrated solutions. Determinations of osmotic pressure of rather concentrated aqueous solutions of calcium ferrocyanide have been carried out at 0° C. by the Earl of Berkeley and Mr. Hartley, who also determined the densities and the relative lowerings of the vapor pressure, thus furnishing all the data required to test equation (33). In the following table some of their results are reproduced, together with the values of the osmotic pressure calculated according to (33).

TABLE XIII. AQUEOUS SOLUTIONS OF CALCIUM FERROCYANIDE AT 0° C.

Grams in 1000 grams water	s	Moles per liter, c	$\frac{ds}{dc}$	$s - c\frac{ds}{dc}$	$\frac{p_0}{p_1}$ found	P calc.	P observed
313.9	1.224	1.001	0.202	1.022	1.033	41.27	41.22
395.0	1.270	1.232	0.192	1.033	1.057	71.22	70.84
428.9	1.287	1.323	0.188	1.038	1.070	87.35	87.09
472.2	1.309	1.438	0.183	1.043	1.092	114.2	112.84
499.7	1.322	1.509	0.180	1.050	1.107	132.8	130.66

It will be evident that equation (33) gives the osmotic pressure even of concentrated solutions with great accuracy. A glance at the column headed $\left(s - c\frac{ds}{dc}\right)$ shows that this expression has a maximum deviation from $s_0 = 1$ of about five per cent, so that the simpler equation (34) would reproduce the osmotic pressures

of the calcium ferryocyanide solutions with an error not greater than five per cent and usually less.

The simple formula, (equation (30)), which we have deduced for dilute solutions, may be tested by means of Pfeffer's experiments with a one per cent sugar solution. The concentration of this solution is very approximately $\frac{1.0}{34\frac{1}{2}} = 0.0292$ moles of sugar per liter. The value of R when the pressure is expressed in cm. of Hg and the volume in liters is $76 \times 0.08207 = 6.273$. The osmotic pressure, P, of this solution according to equation (30) should be $P = 0.0282 \times 6.273 \times T = 0.182\ T$. The following table contains the osmotic pressures at different temperatures as measured by Pfeffer and as calculated according to this formula.

TABLE XIV

$t°$ C.	P observed	P calc.
	cm.	cm.
6.8	50.5	50.9
13.2	52.1	52.1
13.8	52.2	52.2
14.2	53.1	52.3
22.0	54.8	53.7

Since Pfeffer also found that at a given temperature, the osmotic pressure of dilute cane-sugar solutions was proportional to the concentration, we may look on equation (30) as established for dilute solutions.

The resemblance between equation (30) and the equation of state of an ideal gas ($pV = nRT$) is very striking and was first pointed out by van't Hoff.* The osmotic pressure of a dilute solution is equal to the gaseous pressure which the solute would exert if it were an ideal gas and filled the space occupied by the solution. Accordingly all the relations which we have found between the pressure, volume, temperature and molecular weights of gases, hold for the solute in a dilute solution if we substitute osmotic pressure for gaseous pressure. On account of the simplicity of equation (30), many physical chemists in discussing the

* Z. f. physik. Chem., **1**, 481 (1887).

various properties of solutions have related these properties, whenever it was possible, to the osmotic pressure of the solution. And just as the kinetic-molecular theory of gases has shown itself very fruitful in accounting, not only for the pressure but for many other properties of gases, so also attempts have been made with a considerable degree of success to give a kinetic interpretation of osmotic pressure, supposing that the osmotic pressure is due to the motion of the molecules of the solute. Thus if water and an aqueous solution separated by a wall permeable only to the water are in equilibrium, on the basis of the molecular theory the number of molecules passing through the wall per second in one direction must equal the number passing through the wall per second in the opposite direction. The water must therefore exert equal pressures on the two sides of the wall. The extra pressure on the solution side must be due to the molecules of the solute. This in brief is the kinetic view of osmotic pressure. From the point of view adopted in this book, however, the osmotic pressure of a solution is defined, in a purely experimental manner, as equal to $P_2 - P_1$ where P_2 and P_1 are the pressures on the solution and solvent respectively when the two liquids are in equilibrium. A comparison of equations (10a), (15) and (27) or (34) will show that the osmotic pressure of a solution can be expressed very simply in terms of the difference between the boiling-point or freezing-point of the solution and of the pure solvent. Thus if T_b is the boiling-point of the solvent under any pressure, p_0, and if $T = T_b + \Delta T_b$ is the boiling-point of the solution under the same pressure, then the osmotic pressure of the solution at the temperature T_b is

$$P = \frac{L}{M_1 v_1} \cdot \frac{\Delta T_b}{T} = \frac{L}{M_1 v_1} \cdot \frac{\Delta T_b}{T_b + \Delta T_b}. \tag{35}$$

If a solution freezes ΔT_f degrees below the freezing-point T_f of the pure solvent, then the osmotic pressure of the solution at the temperature T_f is given by the relation

$$P = \frac{L_f}{M_1 v_1} \cdot \frac{\Delta T_f}{T_f - \Delta T_f}. \tag{36}$$

If the volume v_1 is expressed in liters and the osmotic pressure, P, in atmospheres, the latent heat of fusion must be converted into

liter-atmospheres. Taking $\frac{L_f}{M_1}$ equal to 79.7 calories, we obtain for aqueous solutions at 0° C.,

$$P = \frac{0.01206}{v_1} \frac{\Delta T_f}{1 - \frac{\Delta T_f}{273}} = \frac{0.01206}{v_1} \Delta T_f \left(1 + \frac{\Delta T_f}{273} \ldots\right). \quad (37)$$

Substituting the value of $\frac{1}{v_1}$ from equation (32), we have

$$P = 12.06 \left(s - c\frac{ds}{dc}\right) \Delta T_f \left(1 + \frac{\Delta T_f}{273} \ldots\right). \quad (38)$$

We can test equation (38) by means of the experimental results of Morse, Frazer and associates,* who determined the freezing-points, densities and osmotic pressures of aqueous solutions of cane-sugar. The results are given in the following table.

TABLE XV. OSMOTIC PRESSURE OF CANE-SUGAR SOLUTIONS AT 0° C.

ΔT_f	Moles of sugar in 1000 grams water	s = density	c = moles per liter	$s - c\frac{ds}{dc}$	P obs.	P calc.
0.195	0.09924	1.0131	0.09724	0.9999	2.46	2.35
0.393	0.1985	1.0257	0.1906	1.0000	4.72	4.75
0.584	0.2978	1.0379	0.2804	1.0001	7.08	7.06
0.784	0.3970	1.0495	0.3668	1.0002	9.44	9.48
0.983	0.4962	1.0607	0.4499	1.0004	11.9	11.9
1.190	0.5954	1.0714	0.5300	1.0006	14.4	14.4
1.390	0.6946	1.0817	0.6071	1.0008	16.9	16.8
1.621	0.7929	1.0916	0.6815	1.0010	19.5	19.7
1.829	0.8931	1.1011	0.7532	1.0013	22.1	22.2
2.066	0.9924	1.1103	0.8225	1.0016	24.8	25.1

As will be seen on examining the column headed $\left(s - c\frac{ds}{dc}\right)$, the value of this function is approximately unity and was so taken in calculating P by means of equation (38). It will also be evident that the osmotic pressure of a solution can be calculated with a considerable degree of accuracy from the lowering of the freezing-point. We should even expect that the simple equation,

$$P = 12.06\, \Delta T_f, \quad (39)$$

* Amer. Chem. Jour., **36**, 91 (1906); **45**, 600 (1911).

would give good results over a considerable range of concentrations in aqueous solutions at 0° C.

The molar latent heat of fusion L_f of course varies with the temperature according to equation (30), Chap. VI. Thus if L_{f_0} is the latent heat at the temperature T_f and L_f is the latent heat at the temperature $T = T_f - \Delta T_f$, then $L_f = L_{f_0} - (C_1 - C_2)\,\Delta T_f$ where ΔT_f is the lowering in the freezing-point. The value of C_1 can be taken as equal to 18 and that of C_2 (referring to 18 grams of ice) as equal to 9. Hence if $L_{f_0} = 79.7 \times 18$ calories, $L_f = 79.7 \times 18\,[1 - 0.0063\,\Delta T_f]$. If this value of L_f is taken in deducing the relation between the osmotic pressure of aqueous solutions and their freezing-points, we shall obtain $P = 12.06\,\Delta T_f\,[1 - 0.0063\,\Delta T_f]\left[1 + \frac{\Delta T_f}{273} + \ldots\right]$ instead of equation (38), assuming $s - c\frac{ds}{dc}$ equal to 1. Therefore a more accurate equation for the relation between the osmotic pressure of aqueous solutions at 0° C. and the freezing-point lowerings is the following:

$$P = 12.06\,\Delta T_f\,(1 - 0.0026\,\Delta T_f). \qquad (39a)$$

As can be easily shown by applying it to the case of cane-sugar solutions at 0° C., equation (39a) will give the osmotic pressure of cane-sugar solutions even more accurately than equation (38).

The relation between the osmotic pressure and other properties of a solution may be deduced from our general conditions of equilibrium. Thus let a system consist of a pure solvent (the first phase) and a solution (the second phase), the two phases being separated by a wall permeable only to the solvent. Let P_1 be the pressure on the solvent, P_2 that on the solution. A study of equations (29), (30), (31), (32), (33), (47), (49), (51) and (56) of Chap. XI will show that the condition of equilibrium in our present system may be written (in place of equation (56))

$$\frac{L_1}{T}\,dT + V_1\,dP_1 - V_2\,dP_2 + B'd\left(\frac{N_2}{N_1}\right) = 0. \qquad (40)$$

In equation (40) L_1 is the heat absorbed when one mole of solvent under the pressure P_1 is transferred through the semi-permeable

membrane to the solution under the pressure P_2; V_1 is the volume of one mole of solvent and V_2 is the increase in volume of a large amount of the solution when one mole of solvent is added to it. V_2 is identical with $M_1 v_1$ of equation (32), this chapter. Even if the solution is concentrated V_2 will not in general differ much from V_1 (compare the column headed $\left(s - c\frac{ds}{dc}\right)$ in the table giving the osmotic pressure of cane-sugar solutions at 0° C.). N_1 and N_2 are the number of moles of solvent and solute in the solution and finally B' is equal to $-N_1\left(\frac{d\Phi_1}{dN_2}\right)_{T,\,P_2,\,N_1}$ $= -N_1\left(\frac{d\Phi_2}{dN_1}\right)_{T,\,P_2,\,N_2}$ (see equations (55) of Chap. XI). Let ΔU be the increase in the total energy of the system when one mole of the solvent goes from the solvent to the solution. If this takes place at constant pressure (say of one atmosphere) the external work is negligible and $\Delta U = -H_d$, the differential heat of dilution by one mole of solvent. But if the solvent is at a constant pressure P_1, and the solution at a constant pressure P_2, the external work done is $P_2V_2 - P_1V_1$ and therefore the heat absorbed is L_1 (of equation (40)) and L_1 is equal to $\Delta U - P_1V_1 + P_2V_2$. We may therefore write

$$L_1 = -H_d - P_1V_1 + P_2V_2, \tag{41}$$

or very approximately (since V_2 and V_1 are nearly equal)

$$L_1 = PV_2 - H_d. \ (P = P_2 - P_1 = \text{osmotic pressure}). \tag{42}$$

Temperature and Composition Constant

If the temperature and composition of our system are kept constant, we can still vary P_1 and P_2 subject to the relation

$$V_2\,dP_2 = V_1\,dP_1 \quad \text{or} \quad dP_2 = \frac{V_1}{V_2}\,dP_1.$$

But since $P = P_2 - P_1$, $dP = dP_2 - dP_1$ and hence

$$dP = \left(\frac{V_1}{V_2} - 1\right)dP_1 = \left(1 - \frac{V_2}{V_1}\right)dP_2, \tag{43}$$

an equation which tells us how the osmotic pressure of a solution in equilibrium with the pure solvent varies with the pressure on the solution or on the solvent. Since, as we have seen, V_1 and V_2 are very nearly equal, the osmotic pressure of a solution is to a great extent independent of the external pressure.

Composition and Pressure P_1 on Solvent Constant

If the pressure on the solvent is kept constant (say at one atmosphere) and if the composition of the solution is not allowed to vary, we have, since $dP = dP_2$, (P_1 = constant),

$$dP = \frac{L_1}{TV_2}\,dT$$

and from equation (42)

$$\left.\begin{aligned} dP &= \left(\frac{P}{T} - \frac{H_d}{TV_2}\right)dT, \\ \frac{dP}{P - \dfrac{H_d}{V_2}} &= \frac{dT}{T}. \end{aligned}\right\} \tag{44}$$

On integration, assuming V_2 and H_d to be independent of the temperature, we obtain

$$P = kT + \frac{H_d}{V_2}. \tag{45}$$

Now, for sufficiently dilute solutions, $H_d = 0$ and, in this case,

$$P = kT \quad \text{and} \quad \frac{dP}{dT} = \frac{P}{T}. \tag{46}$$

We have already found that for a very dilute solution (Raoult's Law being assumed) equation (30) is valid and hence P is proportional to the absolute temperature and $\frac{dP}{dT} = \frac{P}{T}$. But if the heat of dilution of a solution is positive, the osmotic pressure of the solution will be greater and its increase with rise of temperature will be less than would be deduced from equation (30). It is evident then that erroneous results will be obtained by applying the simple equation (30) even when the solutions considered are

fairly dilute, if there is an appreciable heat of dilution. Neglect of this point has vitiated the conclusions drawn by many experimenters in regard to the molecular weights of dissolved substances.

Law of Distribution

If a substance is present in two phases, its partial vapor pressures above each phase must be equal when the system is in equilibrium. Let us assume that the substance is present in each phase in such small proportions that we may consider each phase to be a dilute solution of the substance. Let p_1 be the partial vapor pressure and let x_1 and x_2 be the mole fractions of the substance in the two phases. Then, according to equation (20),

$$x_1 = k_1 p_1 \quad \text{and} \quad x_2 = k_2 p_1 \tag{47}$$

and hence

$$\frac{x_2}{x_1} = k. \tag{48}$$

A substance distributes itself between two phases subject to the condition that the ratio of its mole fractions in the two phases is a constant at a given temperature. It is assumed that the solutions are dilute and that the substance has the same molecular weight in both phases. It is easy to show that for dilute solutions instead of mole fractions we can use concentrations, just as in the deduction of Henry's Law. In fact Henry's Law is a special case of the general law of partition of a substance between two phases.

PROBLEMS

1. At 80° C. benzene has a vapor pressure of 753.62 mm. A solution consisting of 2.47 grams of ethyl benzoate in 100 grams of benzene (molecular weight = 78) has a vapor pressure at 80° C. of 744.36 mm. (*a*) Assuming Raoult's Law, calculate the molecular weight of the dissolved ethyl benzoate. (*b*) By means of equation (27) or (34) calculate the osmotic pressure of the solution, given the density of benzene at 80° C. equal to 0.8145. (*c*) Assuming the solution to have the same density, calculate the osmotic pressure by means of equation (30).

2. The value of λ for 1 gram of benzene at its normal boiling-point (80.2° C.) is 93 calories. Calculate the elevation of the boiling-point pro-

duced by 1 mole of solute (*a*) in 1000 grams of benzene, (*b*) in 1000 cc. of benzene.

3. The latent heat of fusion of benzene is 30 calories per gram. Calculate the lowering of the freezing-point due to 1 mole of solute in 1000 grams of benzene.

4. The density of benzene at its melting-point, (5.4° C.), is 0.8943. The freezing-point of benzene is lowered 0.840 degree by the presence of ethyl benzoate. Calculate the osmotic pressure of the solution at 5.4° C. by means of equation (36). Calculate the composition of the solution.

5. A vessel of 2 liters' capacity contains originally 1 liter of pure water and 1 liter of air at 0° C. and 1 atmosphere. The absorption-coefficients in water at 0° C. are: oxygen, 0.04890; nitrogen, 0.02388; argon, 0.05780. If air is taken as consisting of 78.06 per cent nitrogen, 21.00 per cent oxygen and 0.94 per cent argon, in per cents by volume, calculate the final partial pressures and the final total pressure, the partial vapor pressure of water at 0° C. being 4.58 mm.

6. The vapor pressure of pure water at 25° C. is 23.763 mm. Calculate the vapor pressure at 25° C. of (*a*) 1 per cent urea solution, (*b*) 1 per cent cane-sugar solution. Also calculate the osmotic pressure of each solution.

7. The following table contains the concentrations of I_2 in coexisting phases of water and CCl_4 in moles per liter. The temperature is 25° C. The density of CCl_4 is 1.5843. Find the partition coefficient in terms of concentrations and in terms of mole fractions.

Water	CCl_4
0.0000258	0.002206
0.0000409	0.003483
0.0000638	0.00544
0.0001457	0.01280

8. The vapor pressure of water at 0° C. being 4.579 mm. and that of an aqueous solution containing 86.3 grams of glucose per liter being 4.541 mm., calculate the osmotic pressure of the solution at 0° C.

9. The vapor pressure at 0° C. of an aqueous solution containing 36.52 grams NaCl per liter is 0.09125 mm. less than that of pure water at 0° C. Calculate the osmotic pressure of the solution and also the molecular weight of the solute.

CHAPTER XIV

APPLICATIONS OF THE PHASE RULE III

Equilibrium between Liquid and Solid Phases

Systems of Two Components

On account of the great variety of phenomena met with in a study of the equilibrium between liquid and solid phases in systems of two components, it will be impossible for us to do more than select a few of the more important types for our consideration. We may employ the following rather imperfect scheme of classification to assist us in obtaining a grasp of the most important facts in this field.

Class I. Solid phases are pure substances, insoluble in each other.

Group A. Only two solid phases, the two solid components.

Group B. Solid compounds of the two components are possible.

Division (*a*). The solid compounds of the components on melting change their composition.

Division (*b*). The solid compounds melt without change in composition.

Class II. Solid components are soluble in each other in all proportions.

Class III. Solid components are soluble in each other in limited proportions.

In systems consisting only of liquid and solid phases, change of pressure has very little effect on the equilibrium. Unless otherwise specified we shall suppose the pressure to be constant and sufficiently high to prevent the appearance of a vapor phase. In a system of two components, the number of degrees of freedom is equal to $4 - P$ where P is the number of phases. But if we fix the pressure as constant, there remain then in the systems we

shall study $3 - P$ degrees of freedom. We shall begin with a consideration of systems consisting of the two components, water and silver nitrate. The liquid phase may vary from 100 per cent water to 100 per cent $AgNO_3$; the solid phases will be either ice or pure solid $AgNO_3$ or both. The equilibrium relations are represented graphically in Fig. 27, in which the ordinates are temperatures and the abscissæ represent the composition. Since in general we have several phases present, we shall in general need several curves to indicate the composition of the different phases. The curve giving the composition of the liquid phase will be called the "liquidus" curve; that giving the composition of the solid phase or phases, the "solidus" curve. The "solidus" curve will always be below the "liquidus" curve except that under certain conditions they may touch each other or meet at several points. The curves AC and CB which intersect at the point C give the composition of the liquid phase. A solution whose composition is given by a point on AC is in equilibrium with ice; if the composition is given by a point on CB, the solution is in equilibrium with pure $AgNO_3$. The convention is adopted that the composition of the solid phase in equilibrium with the liquid phase is to be found by drawing a horizontal line from the point on the liquidus curve to the solidus curve. The solidus curve in Fig. 27 consists of the three lines, AD, DE and BE. It is to be noticed however that any point on DE

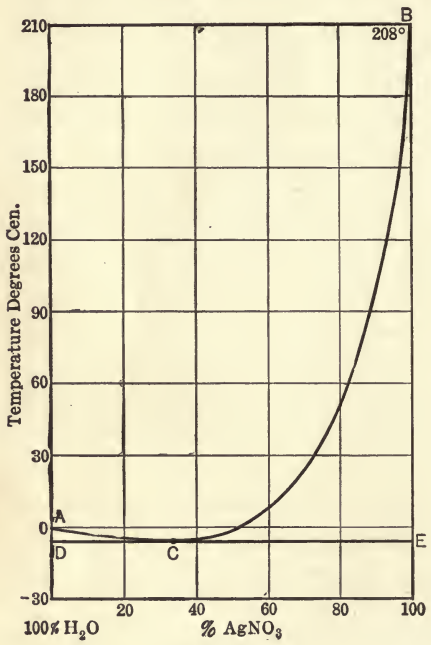


Fig. 27

represents a heterogeneous mixture of the two solid phases whose compositions are given by the points D and E.

Since the pressure is kept constant, our system has $3 - P$ degrees of freedom. The other internal variables may be taken to be the temperature and the composition of the phases. If we have only one phase (say the liquid solution) we shall have two degrees of freedom and therefore the temperature and concentration of the solution may be altered arbitrarily. This corresponds to the region above the curves AC and CB. If we have two phases present, the liquid and one solid, we shall have a univariant system and the concentration will be determined by the temperature. This is illustrated by the curve AC which corresponds to equilibrium between the liquid phase and ice and by the curve BC in which we have the solution and solid $AgNO_3$. Finally we may have three phases present, one liquid and two solid, as represented by point C and this will be an invariant system (at constant pressure). Thus if we start with a solution containing, say, 20 per cent $AgNO_3$ and cool it, we shall reach some point on the curve AC and pure ice will separate out. As ice separates out, the solution becomes richer in $AgNO_3$ and the equilibrium temperature follows the curve AC down to the point C. Similarly if we start with a solution containing 80 per cent $AgNO_3$, we shall have $AgNO_3$ separating out until the point C is reached. When this point has been attained, both ice and silver nitrate will appear as solid phases, and since this is an invariant system there will be no further change in the temperature or the composition of the different phases so long as there are three of them coexisting. The point C also represents in practice the coexistence of the four phases, solution, ice, solid silver nitrate and water vapor, if the pressure on the system is made equal to the vapor pressure, and is therefore a quadruple point. The name "cryohydrate" was originally given to the mixture of ice and salt which is formed at the point C, for at this point the solution freezes without change in temperature or composition and the heterogeneous mixture behaves like a pure substance in having a constant melting-point. AC is usually called a freezing-point curve and BC a solubility curve. There is however no real difference between them.

From the standpoint of the Phase Rule and of thermodynamics, the two components, water and $AgNO_3$, are perfectly equivalent and we should be justified in speaking of $AgNO_3$ as melting at 90° C. when in contact with a solution of a certain composition, just as we speak of ice melting at −5° C. when in equilibrium with the proper solution. Since the point *C* represents the lowest temperature at which solidification takes place from the liquid phase, we may also call it the "eutectic" point, and the solution corresponding to this point, the "eutectic" mixture.

If the two components are not miscible in all proportions in the liquid state, our diagram will be different from Fig. 27. For in this case, if the two components are water and an involatile salt, at a certain point on the curve corresponding to *CB*, two liquid phases will appear. For most purposes, since we usually restrict our consideration of the equilibrium between water and salt to a region of moderate temperatures, we may omit the higher portion of the curve *CB*. Thus our diagram for the system H_2O and KCl would be similar to Fig. 28.

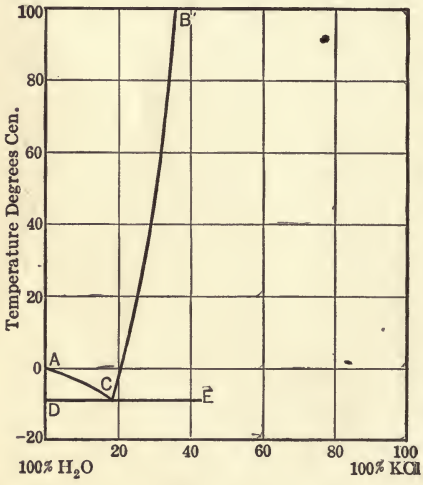


FIG. 28

Let us consider next the melting-point and solubility curves in the system, water and succinic nitrile, investigated by Schreinemakers.* The equilibrium relations will be clear from the diagram in Fig. 29. The freezing-point of water is represented by the point *A*. On cooling a solution containing a small amount of $C_2H_4(CN)_2$, ice will separate at a temperature corresponding to the point on *AC* which represents the composition of the solution. If the solution contains about 5.5 per cent of $C_2H_4(CN)_2$, it will have the composition represented by the cryohydric point

* Zeit. f. physik. Chem., **23**, 418 (1897).

C and both ice and $C_2H_4(CN)_2$ will separate. From solutions whose composition is between that of *C* and *F*, pure solid $C_2H_4(CN)_2$ will separate out on cooling. At the point *F*, corresponding to 18.5° C. and 10.2 per cent $C_2H_4(CN)_2$, we have in equilibrium the three phases, solid $C_2H_4(CN)_2$, and two liquid phases containing 10.2 and 90.2 per cent $C_2H_4(CN)_2$ respectively. If heat is added to this invariant system, the solid phase will gradually disappear at constant temperature, until we have only two phases left. If now the temperature is raised, the two liquid phases will change in composition as given by the curves *FH* and *GH*. The point *H* (55.4° and 51.0 per cent $C_2H_4(CN)_2$) is the critical solution point. The freezing-points of solutions containing between 90.2 and 100 per cent of $C_2H_4(CN)_2$ are given by the curve *BG*, pure $C_2H_4(CN)_2$ being the solid phase which separates out. On cooling a solution corresponding to the point *G* (90.2 per cent $C_2H_4(CN)_2$), we find at 18.5°, solid $C_2H_4(CN)_2$, a liquid phase of composition *G* and a liquid phase of composition *F*. On further cooling, the liquid phase *G* will disappear, leaving the phase *F* and solid corresponding to *E*. On further cooling, the solution will change as given by the curve *FC* until the cryohydric point *C* is reached.

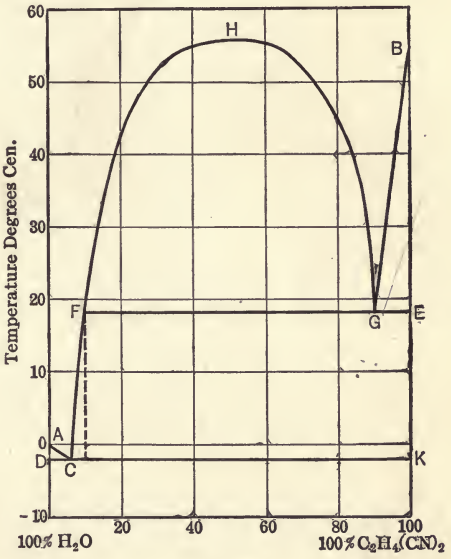


FIG. 29

System of Two Salts

We have examples of many pairs of salts whose melting and freezing curves are similar to those of the system, water and $AgNO_3$. In Fig. 30, we give the liquidus and solidus curves for

systems consisting of KCl and AgCl. Other examples may be found in the numerous diagrams in the Landolt-Börnstein Tabellen. From any liquid mixture of KCl and AgCl, either pure KCl or pure AgCl separates out, except when the mixture is 70 mole per cent AgCl, when the liquid mixture solidifies at the constant temperature of 306° without change in composition. The point *C* is the eutectic point for this system. The interpretation of Fig. 30 is accordingly identical with that given to Fig. 27.

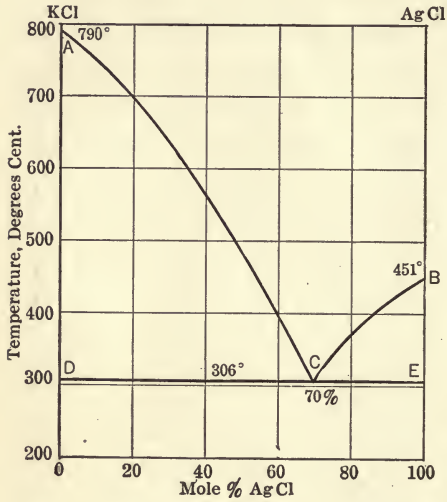


Fig. 30

Systems of Two Metals

The following pairs, Ag and Pb, Bi and Cd, Pb and Sb, also belong to Group A of Class I. In Fig. 31 are given the liquidus and solidus curves for the Pb–Sb system. The interpretation of the diagram is similar to that in the case of the systems H_2O–$AgNO_3$ and KCl–AgCl.

Many examples of binary systems belonging to Group A of Class I may be found among organic substances. We may select as a typical example the two-component system, benzene-chloroform, illustrated in Fig. 32. To the same group belong the binary systems: CH_3Cl–$C_6H_5NH_2$, $C_2H_4Br_2$–C_6H_6, C_6H_6–CH_3CO_2H, C_6H_6–$(C_6H_5)_2NH$, C_6H_6–$C_6H_5NO_2$, $C_2H_4Br_2$–*p*-xylene, and many others.

Class I, Group B, Division (a)

We must now consider the case in which solid compounds of the components are formed. These compounds however are supposed to change their composition on melting. We shall

illustrate Division (*a*) of Group B by means of systems of water and a salt in which solid hydrates are possible. (We may perhaps at this point interpolate the remark that by "melting" we mean the passage of matter from a solid to a liquid phase; the same definition may be used for what is customarily called "dissolving." Similarly by "freezing" or "solidification," we mean the transfer of matter from a liquid to a solid phase and this will include what is usually termed "precipitation".) We shall discuss first of all the system, H_2O–Na_2SO_4, in which the solid phases may be ice, Na_2SO_4, $Na_2SO_4 \cdot 7\,H_2O$, $Na_2SO_4 \cdot 10\,H_2O$. The heptahydrate in presence of solution is a labile or metastable phase and the curve referring to it will be indicated by broken lines. Since the two components do not form a continuous series of liquid solutions, we shall restrict ourselves to concentrations of Na_2SO_4 in which we have a single homogeneous liquid phase. The phenomena met with are illustrated in Fig. 33. From dilute solutions, ice separates out along the curve *AC*. At the cryohydric point *C*, ice and

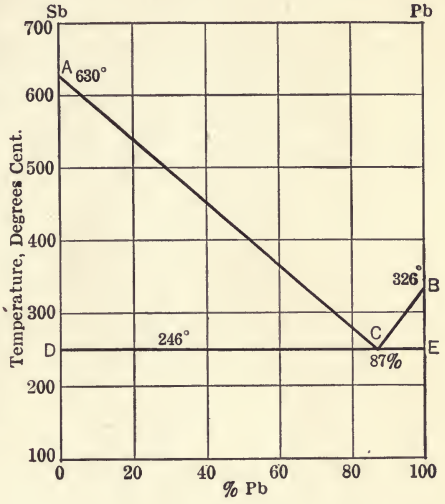


FIG. 31

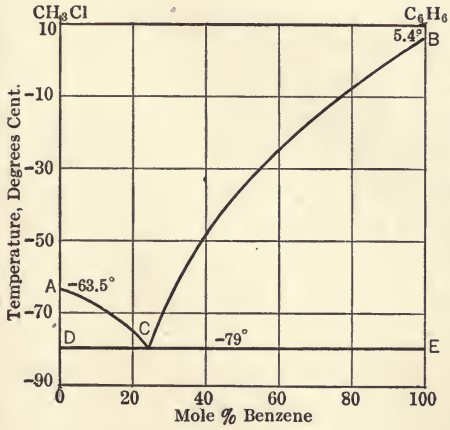


FIG. 32

$Na_2SO_4 \cdot 10\,H_2O$ precipitate. From more concentrated solutions, the solid phase formed is $Na_2SO_4 \cdot 10\,H_2O$ as given by the curve *CE*. The curve *FE* gives the equilibrium between solution and anhydrous Na_2SO_4. The point *E* corresponds to the coexistence of the three phases, solution, Na_2SO_4, $Na_2SO_4 \cdot 10\,H_2O$ and therefore, at constant pressure, this represents an invariant system. Thus addition of heat will increase the quantities of the solution and of Na_2SO_4 and diminish the

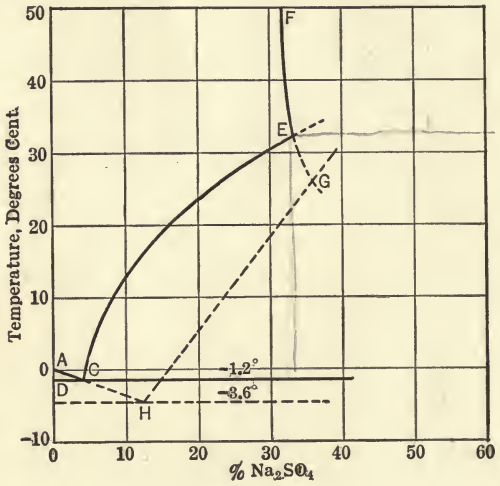


FIG. 33

amount of $Na_2SO_4 \cdot 10\,H_2O$. The temperature corresponding to the point *E* may therefore be called the melting point of $Na_2SO_4 \cdot 10\,H_2O$. It is also called a transition-point, for below this temperature the stable solid phase is the decahydrate and above this temperature, the anhydrous salt. Under certain conditions, the heptahydrate can be obtained; its equilibrium relations are shown by the broken curves.

The melting of one mole of decahydrate is represented by the equation

$$Na_2SO_4 \cdot 10\,H_2O \rightarrow x\,Na_2SO_4 + [(1 - x)\,Na_2SO_4 + 10\,H_2O],$$

where the expression in brackets represents the composition of the solution corresponding to the point *E*. This solution contains 33.2 per cent Na_2SO_4.

In Fig. 34, we have the system H_2O and $Cu(NO_3)_2$ represented. The curve AB represents solutions from which ice separates out on cooling. In the case of solutions represented by BC, CD and DF the solid phases separating out are respectively $Cu(NO_3)_2 \cdot 9H_2O$, $Cu(NO_3)_2 \cdot 6H_2O$ and $Cu(NO_3)_2 \cdot 3H_2O$. The point B is the so-called cryohydric point. The point C is called the transition point between $Cu(NO_3)_2 \cdot 9H_2O$ and $Cu(NO_3)_2 \cdot 6H_2O$, while D is the transition point for the hexahydrate and the trihydrate.

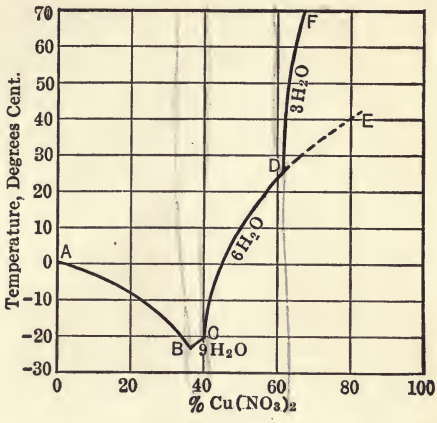


FIG. 34

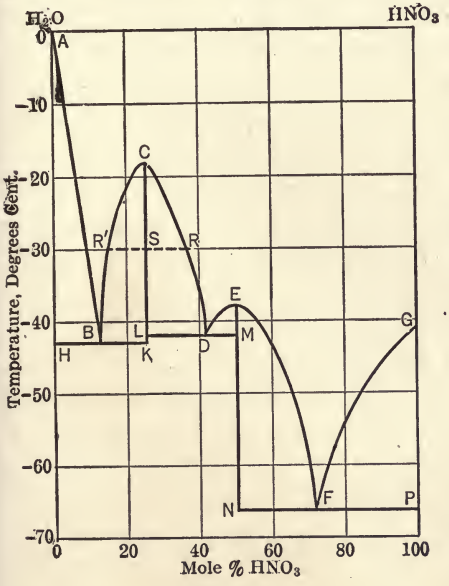


FIG. 35

The system, picric acid-benzene, is analogous to the systems just described. A compound, $C_6H_2(NO_2)_3OH \cdot C_6H_6$, appears as a solid phase, but at 84.3° C. we have a transition point at which it changes into $C_6H_2(NO_2)_3OH$ plus solution.

Class I, Group B, Division (b)

We shall take as our first example of a system belonging to Division (*b*) of Group B of Class I, the binary system, H_2O–HNO_3, represented in Fig. 35. The solid phases possible are ice, $HNO_3 \cdot 3H_2O$, $HNO_3 \cdot H_2O$ and HNO_3. All these substances

melt without change in composition. The coördinates of some of the important points are as follows:

A, 0° C., 0 mole per cent HNO_3;
B, −43° C., 11.96 mole per cent HNO_3;
C, −18.5° C., 25 per cent;
D, −42° C., 40.6 per cent;
E, −38° C., 50 per cent;
F, −66.3° C., 71.9 per cent;
G, −41.2° C., 100 per cent.

The composition of the solid phase which separates out on cooling a solution corresponding to any point on the liquidus curve is obtained by drawing a horizontal line to the solidus curve. Thus if a solution has a composition represented by the point *R*, the solid phase which separates out when the liquid phase is cooled to −30° C. is represented by the point *S* on the solidus curve *CL*. The point *C* corresponds to the compound $HNO_3 \cdot 3\ H_2O$, the point *E* to the compound $HNO_3 \cdot H_2O$. Solutions of these compositions freeze without change in composition and therefore at constant temperature and the corresponding solids melt at constant temperature without change in composition. If we add to a solution having the composition *C* either H_2O or HNO_3, the freezing-point will be lowered and from either solution the hydrate $HNO_3 \cdot 3\ H_2O$ will separate out on cooling. It will be seen that at a given temperature (for example −30° C.) we can have two different solutions, represented by *R'* and *R*, in equilibrium with the same solid phase, $HNO_3 \cdot 3\ H_2O$. We can interpret the curves *BC* and *CD* as giving the solubility of $HNO_3 \cdot 3\ H_2O$ in water, so that we have the interesting result that $HNO_3 \cdot 3H_2O$ has two quite distinct solubilities in water over a considerable range of temperature. This phenomenon is always met with in systems of two components which form solid compounds which melt without producing a phase of a different composition. This will be illustrated by the system H_2O–Fe_2Cl_6 in which a number of hydrates are possible. Here the possible solid phases are: Ice, $Fe_2Cl_6 \cdot 12\ H_2O$, $Fe_2Cl_6 \cdot 7\ H_2O$,

$Fe_2Cl_6 \cdot 5\ H_2O$, $Fe_2Cl_6 \cdot 4\ H_2O$, Fe_2Cl_6. The melting-point and solubility curves are represented in Fig. 36.

The solidus curves have not been drawn, but can be easily applied by the student. The points *B*, *D*, *F* and *H* correspond respectively to pure dodecahydrate, heptahydrate, pentahydrate and tetrahydrate. The points *C*, *E*, *G* and *I* may be described

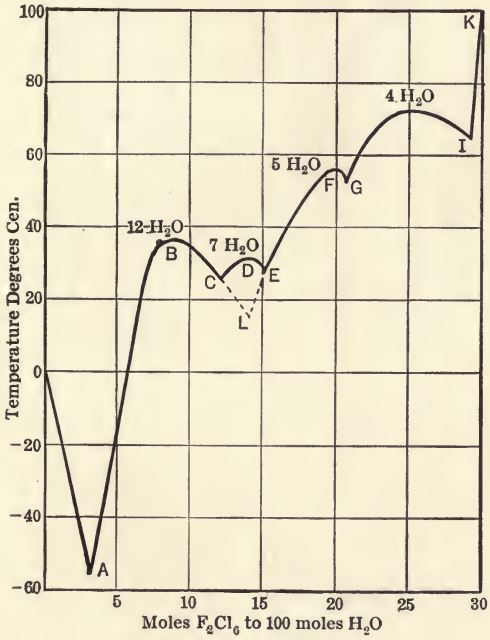


FIG. 36

as eutectic points. The point *L* is the eutectic point between dodecahydrate and pentahydrate in a metastable region.

Similar behavior is shown by many pairs of salts and of metals. It will suffice however to give the curves for the binary system Mg–Sn as an illustration of this behavior. This is done in Fig. 37. The student can readily determine by means of this diagram the nature of the solid phase which will separate out on cooling any liquid mixture of Mg and Sn.

We may finally illustrate Division (*b*) of Group B of Class I by means of systems consisting of organic substances. We may

take as an example the system, phenol-trimethylcarbinol as represented in Fig. 38. In addition to the pure components, we have the solid phases, PA_2 and P_2A, where P and A represent respec-

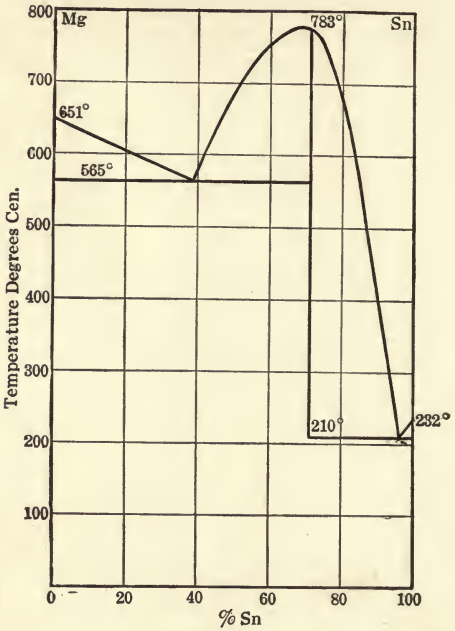


FIG. 37

tively a molecule of phenol and of the alcohol. The coördinates of the principal points in degrees Centigrade and in moles per cent of phenol are as follows:

A,	24.95° C.,	0 per cent.
B,	8.14° C.,	12.6 per cent.
C,	23.3° C.,	33.3 per cent.
D,	4.48° C.,	56.4 per cent.
E,	15.75° C.,	66.7 per cent.
F,	8.5° C.,	75.3 per cent.
G,	40.9° C.,	100 per cent.

Belonging to the same division are the following binary systems: $(C_2H_5)_2O$–C_2H_5I, acetone-phenol, ethyl alcohol-acetaldehyde, acetone-pyrogallol, urea-phenol, benzene-triphenylmethane, and many others.

Class II, Solid Components Soluble in All Proportions

In Class II, we meet with solid solutions, that is, with solids which are physically homogeneous mixtures. We have three types of melting-point curves exactly analogous to the three types of boiling-point curves illustrated in Figs. 20, 21 and 22 of Chap. XII. Type I, in which the freezing-points of all mixtures lie between those of the pure components, is represented by the following binary systems: AgCl–NaCl, $PbBr_2$–$PbCl_2$, $SnCl_2$–$PbCl_2$, Ag–Au, Ag–Pd, Co–Ni, Cu–Ni, Cu–Pd, etc. The general behavior will be illustrated by means of the Cu–Ni diagram given in Fig. 39. A liquid mixture of copper and nickel having the composition represented by the point l on the liquidus curve is gradually cooled. At about 1300 degrees a solid phase having the composition s will separate out. If the cooling is carried out very slowly so that the solid phase always remains homogeneous, the composition of the solid when the last drop of liquid solidifies must be given by the point s' vertically below l and hence the last drop of liquid must have the composition represented by l'. These points also give the final temperature of solidification. If however the

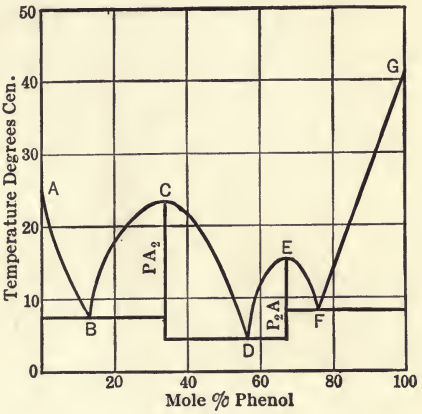


FIG. 38

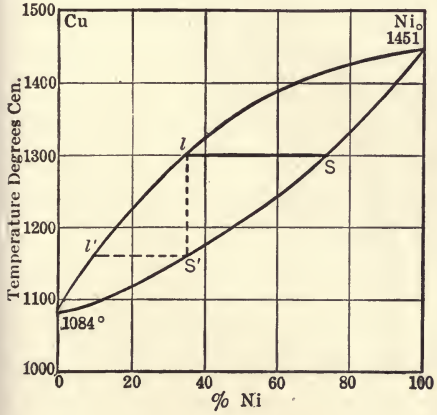


FIG. 39

cooling is not carried out with sufficient slowness, the solid will not have time to become homogeneous and the result will evidently be that the final temperature of solidification will be much lower than we have supposed. In the interpretation of all freezing-point and melting-point diagrams referring to systems in which solid solutions occur, this point must be borne in mind constantly. In general we shall assume that the freezing and melting processes are carried out so slowly that diffusion in the solid solutions is able to maintain the solid phases homogeneous.

Class II. Type II

Very few systems belonging to type II are known, the best investigated one being the binary system: *d*- and *l*-carvoxime. This system is represented in Fig. 40. The points *A* and

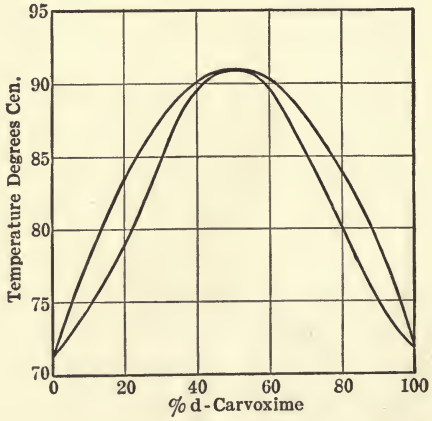


Fig. 40

B are at 72° C. The maximum freezing-point *C* is at 91.4° C. and corresponds to equimolecular proportions of the two components.

Class II. Type III

A large number of binary systems belong to type III, in which a certain mixture has a lower freezing-point than any other mixture and lower than either of the pure components. We may

take as our first example the system $HgBr_2$–HgI_2 represented in Fig. 41. The melting-points of the pure components are 236° C. and 255° C. and the minimum or eutectic point is about 217° C., the mixture containing at this point about 40 mole per cent HgI_2. Assuming that the process of cooling is carried out slowly so that the solid phase is always a homogeneous solid solution, we can predict the behavior of any given mixture when the temperature

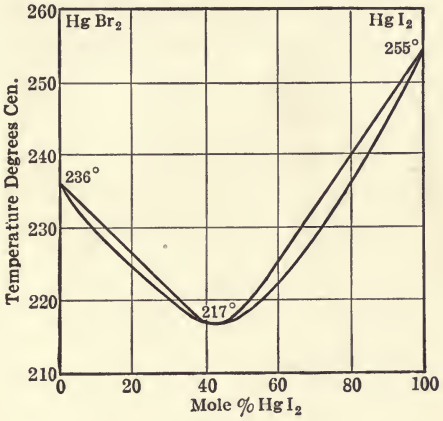


Fig. 41

is lowered. Thus a mixture having the composition l will begin to solidify at 225° C. and the solid phase will have the composition s, that is, will be richer in $HgBr_2$. On further cooling the temperature will fall as the composition of the liquid approaches l' and that of the solid approaches s' and the final temperature of freezing will correspond to the points s' and l'. If the solid phase be removed, as soon as it is formed, from contact with the liquid (a process analogous to what happens in ordinary distillation) the composition of the liquid will reach that given by the point C after which solidification will take place without any change in composition or temperature. Approximately the same result will be attained on rapid cooling, for under these circumstances, the portions of the solid phase formed in the earlier stages will be practically removed from contact with the liquid by being surrounded by solids richer in HgI_2.

Fractional Crystallization of Solid Solutions

Just as by fractional distillation a more or less complete separation of liquids soluble in each other can be effected, so by fractional crystallization we can effect a separation of the components in a solid solution. In the case of solid solutions belonging to type I (Fig. 39) a practically complete separation into the two pure components is possible. In the case of solid solutions with a minimum freezing- or melting-point, fractional crystallization will effect a separation into the eutectic mixture and into one of the pure components. Thus fractional crystallization of a mixture containing 20 mole per cent HgI_2 and 80 mole per cent $HgBr_2$ would ultimately result in pure $HgBr_2$ and the eutectic mixture.

As additional examples of binary systems similar to the system $HgBr_2$–HgI_2, we may mention the following: $CaCl_2$–$MnCl_2$; $CaSiO_3$–$MnSiO_3$; $CdSiO_3$–$ZnSiO_3$; KCl–KBr; KBr–KI; and among the alloys, Cu–Au; Cu–Mn; Fe–V; Mn–Ni. Details in regard to these systems (as well as many others) may be found in Landolt-Börnstein Tabellen.

Class III. Solid Components Partially Soluble in Each Other

We now come to consider binary systems in which the possible solid phases are not soluble in each other in all proportions. We shall be able to give but a few examples out of the large number of systems belonging to this class. We may divide Class III into two large groups; the first one including systems in which there is a eutectic or minimum freezing-point; the second group, those in which all freezing-points are intermediate between those of the pure components. In the latter case we have a transition point instead of a eutectic. We shall take as our first example of a system with a eutectic point, mixtures of KNO_3 and $TlNO_3$, the curves for which are given in Fig. 42. On cooling a liquid mixture having the composition *l*, a solid solution of composition *s* will separate out. On further cooling, if the original mixture was richer in $TlNO_3$ than corresponds to the point *D*, the composition of the liquid will follow the curve to the point *C*. At the temperature corresponding to this point, two solid solutions

corresponding to *D* and *E* separate out at constant temperature until all the liquid has solidified. If the temperature is lowered below 182° C., the two solid solutions in equilibrium with each other change their composition as indicated by the dotted lines. Any solid having a composition intermediate between *D* and *E* will consist at 182° C. of two solid phases, the composition of the phases being given by *D* and *E*. Similar behavior is shown by the system KNO_3 and $NaNO_3$. KNO_3 melts at 339° C., $NaNO_3$ at 308° C., the eutectic temperature is 218° C. and the

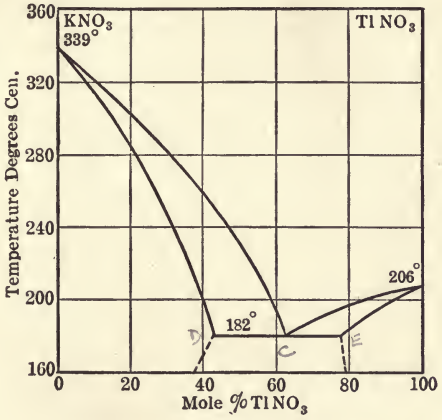


FIG. 42

liquid phase at the eutectic point contains about 51 mole per cent KNO_3. At the eutectic temperature we can have solid solutions containing from 0 up to 20 mole per cent KNO_3 and from 87 up to 100 mole per cent KNO_3.

The system, naphthalene-monochloracetic acid, also belongs to this group. Among the alloys, we may mention the binary systems, Cu–Ag; Au–Ni; Bi–Pb; Sn–Pb. The system Bi–Pb is represented in Fig. 43. The interpretation of the diagram may be left to the student.

Class III. System has a Transition Point.

A binary system at constant pressure is invariant when three phases coexist, e.g., a liquid phase and two solid phases. In the systems we are now considering in which the solid components

are soluble only to a limited extent in each other, the two solid phases will be saturated solid solutions. If the temperature corresponding to this invariant system is below the melting-point of either component, the system has as we have seen a eutectic point. We now proceed to consider the case in which the temperature corresponding to the invariant system is intermediate between the melting-points of the two components and is then called a transition temperature. The following systems belong to Class III and exhibit a transition point: AgCl–LiCl; $MgSiO_3$–$MnSiO_3$; Cd–Hg; *p*–$C_6H_4I_2$–*p*–C_6H_4ClI; *p*–$C_6H_4(NO_2)Cl$–*p*–$C_6H_4(NO_2)Br$. The behavior of the system Cd–Hg is shown

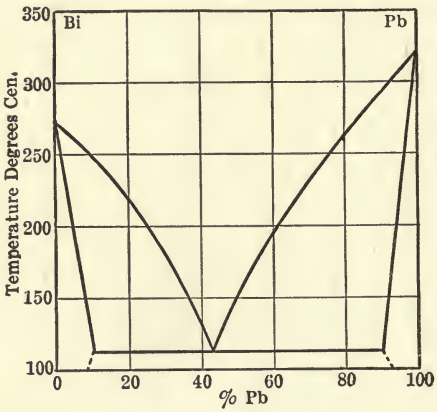


FIG. 43

diagrammatically in Fig. 44. The points *C*, *D* and *E* represent respectively 51, 62.7 and 65.2 per cent cadmium at a temperature of 182° C. The dotted lines *DF* and *EG* represent the composition of the two saturated solid solutions of cadmium and mercury. If we start with a solution whose composition is represented by the point *a*, at a certain temperature a solid phase rich in cadmium will separate out, the temperature of solidification will fall forty or fifty degrees and we shall have finally a homogeneous solid solution of composition *a*. If we start with a solution *b* of composition intermediate between *D* and *E*, the temperature of solidification will fall to 182° C. when the solid phase will have the composition *E* and the liquid phase the composition *C*. If

more heat is extracted from the system, the temperature will remain constant, but the homogeneous solid phase *D* will be formed from the liquid phase and from phase *E*. This will take place at the constant temperature, 182° C. When the liquid phase has entirely disappeared, we shall have the two solid phases *D* and *E* coexisting in amounts depending on the composition of

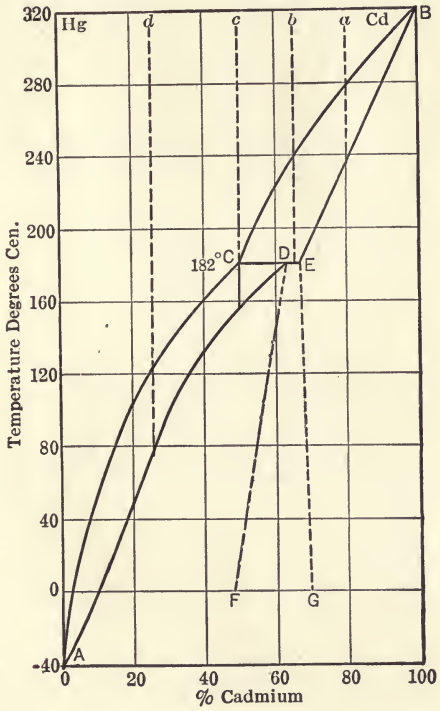


FIG. 44

the original solution. On further cooling, the composition of the two saturated solid solutions will change in accordance with the dotted curves *DF* and *EG*. If we cool a liquid whose composition is intermediate between *C* and *D*, when the temperature 182° C. is reached, the phase *E* will disappear and the phase *D* will be formed. (Hence this temperature is called a transition temperature for the two solid solutions.) On further cooling we shall obtain a homogeneous unsaturated solid solution which however

at low temperatures will break up into two saturated solid solutions the composition of which is given by the dotted lines. On cooling a solution of composition *c*, the behavior will be similar except that the amount of phase *E* formed will be zero or negli-

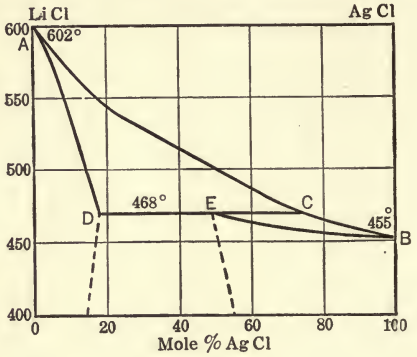


FIG. 45

gible. Finally if we cool a solution of composition *d*, the process of solidification will extend over a rather large temperature-interval and we shall finally have at ordinary temperatures an unsaturated homogeneous solid solution of the composition *d*.

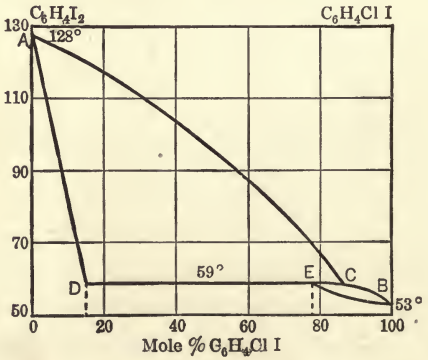


FIG. 46

This case has been discussed in some detail so that it will be sufficient to give the diagrams only for the systems, AgCl–LiCl and *p*–$C_6H_4I_2$–*p*–C_6H_4ClI.

Ternary Systems

On account of the great complexity of phenomena observable in the case of three-component systems, we shall have to be content with a discussion of some of the simpler cases. For more detailed treatment the reader may be referred to Findlay's Phase Rule and its Applications. The number of degrees of freedom in a ternary system is $5-P$. It is possible therefore to have a maximum of five phases coexisting at what is called a quintuple point which would represent an invariant system. The maximum number of degrees of freedom will be four (since we must have at least one phase) and the four internal variables of the system

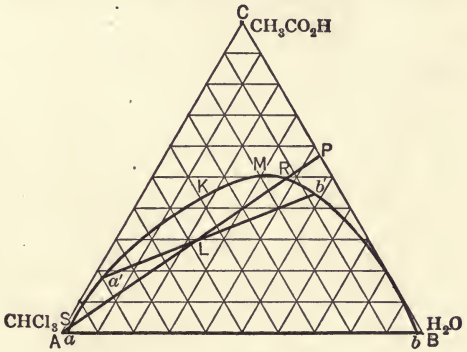


FIG. 47

will be T, p and the two ratios of two of the components to the third in any phase.

We shall begin with a study of the equilibrium relations of three components which are all liquid at the temperatures considered. The three chief cases to be examined are those in which the three components form respectively one, two and three pairs of partially miscible liquids. Examples of the first case are: chloroform, acetic acid and water; ether, water and alcohol; chloroform, water, alcohol; benzene, water and alcohol; molten lead, molten zinc, molten silver. Thus at ordinary temperatures, water and chloroform are but slightly soluble in each other while both water and chloroform will mix with acetic acid in all proportions. The composition of a ternary mixture is best represented by means of a triangular diagram as in Fig. 47 which

gives the equilibrium relations in the system, $CHCl_3$,H_2O and CH_3CO_2H.*

If in this system we maintain the temperature and pressure constant, we shall have left $3-P$ degrees of freedom. In case our system is restricted to one homogeneous phase, it will have two degrees of freedom and will be represented by some point in a "region." If our system consists of two liquid phases, it will be a univariant system and will be represented by a point on a "curve," the curve *aKMb*. The length of each side of the equilateral triangle is set equal to 100 and the point *A* represents 100 per cent *A* or pure *A*. The per cent of *A* in a mixture represented by any point *N* is found as follows: through *N* draw a straight line to the side opposite *A*, parallel to either of the other two sides; the length of this line gives the percentage of *A* in the mixture. In the same way the percentages of *B* and *C* in the mixture are determined. Our diagram then represents a system of three components at the constant temperature, 18° C. and constant pressure. If we restrict our consideration to liquid phases only, all we need know about the pressure is that it is sufficiently great to keep the phases liquid. If to pure chloroform we add water we shall have at first a homogeneous solution, but very soon the chloroform will be saturated with water giving a solution of the composition represented by the point *a*. Further addition of water gives us two conjugate solutions represented by the points *a* and *b*. If we start with a certain mixture of CH_3Cl and acetic acid and add water, we shall have a homogeneous solution until the point *a'* is reached when further addition of water gives us the two conjugate ternary solutions, *a'* and *b'*. The line joining *a'* and *b'* is called a tie-line which in general is not parallel to the base-line *AB*. With solutions containing more and more acetic acid, the tie-lines become shorter and shorter until they shrink to a point *K*, which therefore represents the point where the two conjugate ternary solutions become identical. The point *K* is therefore a critical point although it is not in general at the summit of the curve. Any point in the region outside the curve *aKb* represents a homogeneous mixture, while any point inside

* C. R. A. Wright, Proc. Roy. Soc., **49**, 174 (1891); **50**, 375 (1892).

the curve represents a mixture which will break up into two conjugate liquid phases. Thus if the three components are put together so that the composition of the mixture would be represented by the point L, the mixture will form two liquid layers of the composition given by the end-points a and b' of the tie-line going through the point L. An important property of the diagram may be illustrated as follows: the line AP cuts the curve aKb in the points S and R. It can be shown that in all mixtures represented by points on the line AP, the ratio of C to B or of acetic acid to water is constant and given by the ratio $\frac{PB}{PC}$. If then to a mixture of water and acetic acid of the composition P we add chloroform, we shall have from P to R a series of homogeneous solutions; from R to S we shall have a series of heterogeneous mixtures of the two conjugate solutions and finally from S to A, homogeneous solutions again. If we start with a solution which contains a greater per cent of acetic acid than corresponds to the critical point K, but less than is represented by the point M, it is possible, by adding proper amounts of the three components, to keep the per cent of acetic acid constant and yet travel in a horizontal line from a homogeneous region through the heterogeneous area and then into a homogeneous region again. This phenomenon is called retrograde solubility and is somewhat analogous to retrograde condensation near the critical point in the case of mixtures of two components. The diagrams for the systems: H_2O, ether and C_2H_5OH and Zn,Pb and Ag are similar to the one just described.

Figure 47 represents a ternary system at constant pressure and at a given temperature. The graphic representation of the behavior of these systems at different temperatures requires a space diagram. Thus if we represent temperatures on a vertical axis perpendicular to the triangle ABC of Fig. 47, we obtain the isothermal diagram by drawing a horizontal plane. In the space diagram, the homogeneous region would become a volume, the curve aKb would become a surface and the point K would be represented by a curve.

The second group of ternary systems of three liquids consists

of those in which there are two pairs of partially miscible liquids. Thus water and alcohol are miscible in all proportions, but water and succinic nitrile and alcohol and succinic nitrile are only partially miscible. Such a system is represented in Fig. 48. Any

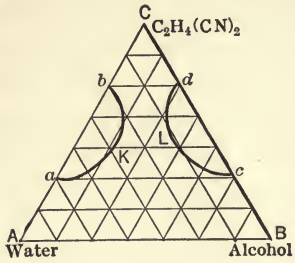


Fig. 48

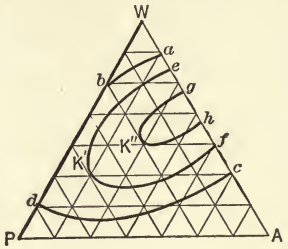


Fig. 49

point on the diagram inside of the curves *aKb* or *cLd* represents a heterogeneous system of two ternary solutions; any other point a homogeneous ternary solution. The curves *aKb* and *cLd* will of course change their position as the temperature is changed. This may be illustrated by the diagram for water, aniline and phenol represented in Fig. 49 where the components are indicated by their initial letters. The curves *ab*, *cd* refer to a temperature

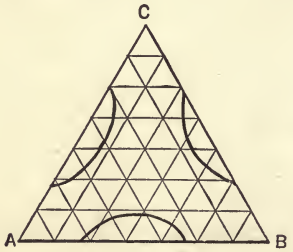


Fig. 50

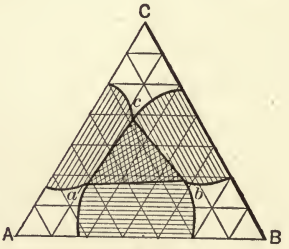


Fig. 51

of 50° C., the curve *eK'f* to 95° C. and *gK''h* to a temperature of 148° C. The interpretation of the diagram may be left as an exercise to the student.

In the third group of ternary systems of three liquids, we have three pairs of partially miscible liquids. The equilibrium relations are represented in Figs. 50 and 51. Fig. 50 represents the case in which the system always consists of either one or two

liquid phases. At lower temperatures it sometimes happens that the curves broaden out and give the diagram of Fig. 51. If the mixture has a composition represented by a point in the clear spaces near the corners of the diagram, the mixture will form a single homogeneous solution. If the representative point lies in any of the quadrilateral areas, the mixture will form two liquid layers and if finally the representative point is within the triangular area, the mixture will break up into three layers of the composition *a*, *b* and *c*. Water, ether and succinic nitrile may be given as an example of a system which can form three liquid phases.

Similar diagrams may be used in the case of ternary systems when some of the components are solid. In illustration of this, we shall consider briefly the ternary system: water plus two salts with either a common positive or a common negative radical, e.g., H_2O–NaCl–KCl. In this case the salts do not form a com-

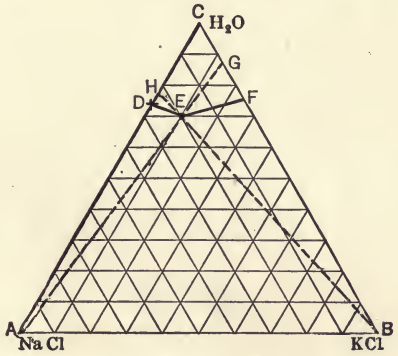


FIG. 52

pound and do not form a solid solution. At any given temperature and pressure, for example, 20° C. and 1 atmosphere, the diagram for this system will be somewhat like Fig. 52. Point *D* represents a saturated solution of NaCl in water (26.4 per cent NaCl, 73.6 per cent H_2O), *F* a saturated solution of KCl in water (25.5 per cent KCl, 74.5 per cent H_2O), *DE* represents ternary solutions in equilibrium with solid NaCl, the curve *FE* solutions saturated with KCl, and the point *E*, a ternary solution saturated with both salts (20.1 per cent NaCl, 10.4 per cent KCl, 69.5 per

cent H_2O). Any point inside the area *CDEF* represents a homogeneous ternary solution. If to a solution of H_2O and NaCl of the composition *H*, KCl is added, the representative point moves along the straight line *HEB*. If NaCl is added to a solution whose composition is given by the point *G*, the representative point moves along the line *GEA*. Therefore if we put water, NaCl and KCl together so that the composition will be given by a point in the area *BEF*, the system will consist of solid KCl and a solution whose composition is given by the point on the line *EF* obtained by drawing from *B* to *EF* a line through the given point in the area *BEF*. Similarly a point in the area *AED* corresponds to solid NaCl and a ternary solution whose composition is given by a point on the curve *DE*. And finally, if our representative point is in the area *AEB*, the system will consist of solid NaCl, solid KCl and the ternary solution *E* which is saturated with both salts. Fig. 52 is an isothermal diagram. If we desire to represent the behavior of our system at different temperatures, we must either use a space diagram or more simply draw in the Fig. 52 curves for different temperatures.

The diagrams become more complicated if the salts can form double compounds or if hydrates are possible or finally if the salts form solid solutions. Further details in this connection may be sought in Findlay's Phase Rule or other similar treatise.

PROBLEMS

1. Using Fig. 29 and the data given in connection therewith, describe in detail what will happen on supplying heat to the following mixtures of ice and $C_2H_4(CN)_2$ originally at $-10°$ C.; namely, mixtures containing 5, 8, 25 and 95 per cent $C_2H_4(CN)_2$.

2. From the data in connection with the system Na_2SO_4–H_2O, determine the amount of Na_2SO_4 and of solution formed when one mole of $Na_2SO_4 \cdot 10\,H_2O$ disappears at the transition temperature.

3. What phase or phases will separate out on cooling an aqueous solution of HNO_3 containing 65 per cent HNO_3 by weight?

4. Describe the phenomena which would be observed on cooling mixtures of Mg and Sn containing 20, 60, 85 and 99 per cent Sn.

5. At what temperature approximately will a mixture of phenol and trimethylcarbinol containing 45 per cent by weight of phenol begin to solidify,

what will be the final temperature of solidification and what will be the solid phase or phases formed?

6. Describe the phenomena encountered on cooling very slowly mixtures of Bi and Pb containing 5, 20, 60 and 95 per cent Pb.

7. Describe the behavior which would be observed on heating very slowly solid mixtures of LiCl and AgCl containing 10, 40, 60 and 90 mole per cent of AgCl.

8. What will be observed on adding acetic acid in increasing amounts to a mixture of 50 grams chloroform and 50 grams water?

9. What will be observed on adding water in increasing amounts to a mixture of 50 grams chloroform and 50 grams acetic acid?

10. According to Fig. 48, what will be observed on adding increasing amounts of succinic nitrile to mixtures of water and alcohol containing (*a*) 50 per cent alcohol, (*b*) 95 per cent alcohol?

11. In a triangular diagram, if (x_1, y_1, z_1) and (x_2, y_2, z_2) are the coördinates of two fixed points and if (x, y, z) are the coördinates of any point on the straight line passing through the two given points, then $\frac{x - x_1}{x_1 - x_2} = \frac{y - y_1}{y_1 - y_2} = \frac{z - z_1}{z_1 - z_2}$ where $x_1 + y_1 + z_1 = x_2 + y_2 + z_2 = x + y + z = 100$. Find the composition of the solutions corresponding to the points *H* and *G* in Fig. 52. If *x*, *y*, *z* refer respectively to NaCl, KCl and H_2O show that the equation for the line *DE* (assumed to be straight) is $x + 0.606\,y = 26.4$ and for the line *EF* is $y + 0.751\,x = 25.5$.

12. What will be the final state on mixing 10.05 grams NaCl, 55.20 grams KCl and 34.75 grams water and what will be the amounts of each phase?

13. What will be the final state on mixing equal weights of NaCl, KCl and H_2O at 20° C.?

14. Determine the composition and mass of the phases resulting on mixing 5 grams NaCl, 55 grams KCl and 40 grams H_2O at 20° C.

15. Show that, using a triangular diagram for a system of three components *A*, *B* and *C*, the proportion of *B* to *C* is the same in all mixtures represented by points on a straight line passing through the corner *A*.

CHAPTER XV

CHEMICAL EQUILIBRIUM

Gaseous Systems

In Chap. IX we discussed the conditions of thermodynamic equilibrium in a system subject to various constraints and found that the conditions could be expressed by saying that some function of the system (such as the entropy, free energy or thermodynamic potential) has a maximum (or minimum) value when equilibrium prevails. Now these functions are determined by the temperature and pressure and the quantities of the various components of a system so that if the thermodynamic potential (or free energy or entropy) of a system is a known function of the variables just mentioned, then the thermodynamic behavior of the system can be readily predicted. As a matter of fact, the entropy, free energy and thermodynamic potential of ideal gases are given by simple equations (see Chap. VIII and Problem 9 of Chap. IX). Moreover in Chap. XIII, we found an expression for the thermodynamic potential of a dilute solution. In this chapter it will be part of our work to show somewhat more explicitly how the state of equilibrium depends on the quantities of the various substances present, firstly, when all the substances are ideal gases, and secondly, when the system is a dilute solution.

If substances which can react with one another are brought together, it will be found that in general, when all change seems to have ceased, the original substances are still present, although their concentrations may be extremely small. We say that the original and final substances are in chemical equilibrium. The system will of course be in thermodynamic equilibrium but we employ the expression "chemical equilibrium," not because it is something different from thermodynamic equilibrium, for it is

not, but because our main concern is with the relative amounts of the various substances present at equilibrium. In other words, we are especially interested in determining the extent to which a given chemical reaction will take place and in finding out how the final state of equilibrium depends, not only on the temperature and the pressure, but on the concentrations of the reacting substances.

Let us suppose that we have the three gases, H_2, O_2 and H_2O at such a temperature that no appreciable chemical interaction occurs even in a long period of time. The system consists then of three independent components in one phase and hence has four degrees of freedom. Representing the concentrations of the three substances by c_1, c_2 and c_3, the phase rule tells us that the total pressure (for example) is a function of four independent internal variables or

$$p = f_1(c_1, c_2, c_3, T). \tag{1}$$

Hence we may also write

$$c_3 = f_2(c_1, c_2, p, T); \quad c_2 = f_3(c_1, c_3, p, T). \tag{2}$$

Let us now suppose that the temperature of our system is raised so that a chemical reaction takes place between the hydrogen, oxygen and water vapor. This reaction leads to a state of chemical equilibrium in which we still have the three substances present. We now have however a system of but two independent components, for at a given temperature and pressure, the concentration of the water vapor is fixed when the concentrations of the hydrogen and of the oxygen are fixed. Our system now has but three degrees of freedom so that we may write:

$$\begin{aligned} p &= f_1(c_1, c_2, c_3) = f_2(c_1, c_2, T) \\ c_2 &= f_3(c_1, p, T); \quad c_3 = f_4(c_1, p, T) \\ T &= f_5(c_1, c_2 c_3). \end{aligned} \tag{3}$$

In other words, all the internal variables of the system are functions of any three internal variables. In this particular case we may take c_1, c_2 and c_3 as the three variables and we find that p and T are functions of c_1, c_2 and c_3. We shall find that another characteristic function of the system, the equilibrium constant, is

determined by any three variables, for example by the values of c_1, c_2 and c_3 at equilibrium. We shall now proceed in a general way to determine the value of the equilibrium constant as a function of the internal variables of a gaseous system.

The system we are to examine may consist of a mixture of a number of ideal gases, whose mole numbers are n_1, n_2, n_3, etc., whose partial pressures are p_1, p_2, p_3, etc., whose concentrations and mole fractions are c_1, c_2, c_3, etc., and x_1, x_2, x_3, etc., and whose temperature and total pressure are T and p. The energy of an ideal gas depends only on its temperature and is independent of its pressure so that the total energy of our mixture is the same as if the gases were in the pure state at the same temperature. The entropy and thermodynamic potential of a gas depend on two variables, and in the case of a mixture the entropy and thermodynamic potential of any component of the mixture are equal to the entropy and potential of that component in the free state at the same temperature as that of the mixture and at a pressure equal to its partial pressure in the mixture. Hence we may, if we desire, consider our mixture of gases separated into the individual components under their respective partial pressures without change in the total energy, entropy or thermodynamic potential (see Chap. VIII on the entropy of a mixture of ideal gases and also equations (14) and (15) of Chap. VIII). If U_1, S_1 and Φ_1 are the energy, entropy and thermodynamic potential of one mole of gas 1, then we have

$$\Phi_1 = U_1 - TS_1 + p_1V_1 = U_1 - TS_1 + RT, \tag{4}$$

and, moreover,

$$\begin{aligned} U_1 &= C_{v_1}T + b_1; \quad U_1 + RT = C_{p_1}T + b_1, \\ S_1 &= C_{p_1}\log T - R\log p_1 + k_1 = C_{p_1}\log T - R\log p \\ &\quad + k_1 - R\log x_1, \\ \Phi_1 &= T(C_{p_1} - C_{p_1}\log T + R\log p_1 - k_1) + b_1 \qquad (5) \\ &= T(C_{p_1} - C_{p_1}\log T + R\log p - k_1) + RT\log x_1 + b_1. \end{aligned}$$

The total thermodynamic potential of the mixture of gases will be

$$\begin{aligned} \Phi &= n_1\Phi_1 + n_2\Phi_2 + n_3\Phi_3 + \cdots \\ &= \sum n_1(C_{p_1}T - C_{p_1}T\log T + RT\log p - k_1T + b_1) \\ &\quad + RT\sum n_1\log x_1. \end{aligned} \tag{6}$$

Chemical Equilibrium at Constant Temperature and Pressure

According to equation (33) (Chap. IX) our system will be in equilibrium at constant temperature and pressure if for any virtual change compatible with the fixed conditions, the following relation holds, viz.:

$$\delta\Phi = 0. \tag{7}$$

We shall consider as a virtual change an infinitesimal change in the mole numbers n_1, n_2, n_3, etc., corresponding to the possible chemical reaction between the gases. The equation for the chemical reaction we shall write as follows:

$$\nu_1 A_1 + \nu_2 A_2 + \nu_3 A_3 + \cdots = 0, \tag{8}$$

where A_1, A_2, A_3, etc., are the molecular formulas of the different gases and ν_1, ν_2, ν_3, etc., represent the number of moles concerned in the chemical change, positive when they refer to the formation of a substance, negative when they refer to the disappearance of a substance. Thus the equation of the union of hydrogen and oxygen to form water would be written

$$-2\,H_2 - O_2 + 2\,H_2O = 0, \tag{9}$$

in which $\nu_1 = -2$, $\nu_2 = -1$; $\nu_3 = 2$. Or we might say that in an equation written in the customary manner, the coefficients on the right-hand side of the equation are to be taken as positive, those on the left-hand side as negative.

Our virtual chemical change will consist in the mole numbers n_1, n_2, n_3 etc., suffering the virtual changes δn_1, δn_2, $\delta n_3 \cdots$ where according to equation (8)

$$\delta n_1 : \delta n_2; \quad \delta n_3 : \cdots = \nu_1 : \nu_2 : \nu_3 : \cdots. \tag{10}$$

Applying our condition of equilibrium at constant temperature and pressure as given in equation (7), we have from equation (6)

$$\delta\Phi = \sum \delta n_1 (C_{p_1} T - C_{p_1} T \log T + RT \log p - k_1 T + b_1) + RT \sum \delta n_1 \cdot \log x_1 + RT \sum n_1 \delta \log x_1 = 0. \tag{11}$$

Now, since $\frac{n_1}{x_1} = \frac{n_2}{x_2} = \frac{n_3}{x_3} = \cdots = (n_1 + n_2 + n_3 + \cdots)$, we have

$$\sum n_1 \delta \log x_1 = \sum \frac{n_1}{x_1} \delta x_1 = (n_1 + n_2 + n_3 + \cdots)(\delta x_1 + \delta x_2 + \delta x_3 + \cdots).$$

But, since $x_1 + x_2 + x_3 + \cdots = 1$, $\delta x_1 + \delta x_2 + \delta x_3 + \cdots = 0$, and hence

$$RT\sum n_1 \, \delta \log x_1 = 0.$$

If in place of δn_1, δn_2, etc., we substitute the finite quantities ν_1, ν_2, etc., as given by equation (10), equation (11) becomes

$$\sum \nu_1 \log x_1 = -\frac{\sum \nu_1 (C_{p_1}T - C_{p_1}T \log T + RT \log p - k_1 T + b_1)}{RT}. \tag{12}$$

When the temperature and pressure are constant, the expression on the right in (12) is constant and we shall represent it by $\log K_x$, so that

$$\left.\begin{aligned} \log K_x &= \sum \nu_1 \log x_1 \\ K_x &= x_1^{\nu_1} \cdot x_2^{\nu_2} \cdot x_3^{\nu_3} \cdots \end{aligned}\right\} \text{ at equilibrium.} \tag{13}$$

We shall call K_x the equilibrium constant in terms of the mole fractions of the substances at equilibrium. We see from equation (12) that K_x is a function of T and p. Thus

$$RT\left(\frac{d \log K_x}{dp}\right)_T = \frac{-\sum \nu_1 RT}{p} = -\Delta V,$$

$$\left(\frac{d \log K_x}{dp}\right)_T = \frac{-\Delta V}{RT}, \tag{14}$$

$$\left(\frac{d \log K_x}{dT}\right)_p = \frac{\sum \nu_1 (C_{p_1}T + b_1)}{RT^2}. \tag{15}$$

Now, from equations (5), $U_1 = C_{v_1}T + b_1$, and since $C_{p_1} = C_{v_1} + R$,

$$\sum \nu_1 \, (C_{p_1}T + b_1) = \sum \nu_1 U_1 + \sum \nu_1 RT = -H_v + \sum \nu_1 RT.$$

But $-H_v + \sum \nu_1 RT = -H_p$ (see equations (15) and (16) Chap. VI). We have therefore the following equations for the dependence of the equilibrium constant K_x on the temperature and the pressure:

$$\left(\frac{d \log K_x}{dp}\right)_T = \frac{-\Delta V}{RT} = \frac{-\sum \nu_1}{p}, \tag{16}$$

$$\left(\frac{d \log K_x}{dT}\right)_p = \frac{-H_p}{RT^2}. \tag{17}$$

If a reaction takes place at constant temperature and pressure with an increase in the total volume, an increase in pressure will diminish the value of the equilibrium constant K_x, and therefore increase the mole fractions of the original substances. Similarly from equation (17) we see that an increase in the temperature of a system in equilibrium will favor the endothermic process.

Evidently from equation (16) a change in the pressure only will not affect the value of K_x if $\sum \nu_1 = 0$, that is, if the number of moles disappearing in the reaction is equal to the number formed.

We may also define equilibrium constants in terms of the partial pressures or the concentrations of the substances at equilibrium. Thus if we set

$$\log K_p = \sum \nu_1 \log p_1 \text{ (at equilibrium)}, \tag{18}$$

we have

$$\begin{aligned} \log K_p &= \sum \nu_1 \log p_1 = \sum \nu_1 \log x_1 + \sum \nu_1 \log p, \\ &= \log K_x + \sum \nu_1 \log p. \end{aligned} \tag{19}$$

Hence at constant temperature and pressure, since K_x is a constant, so also is K_p. From equation (12)

$$\log K_p = -\frac{\sum \nu_1 (C_{p_1} T - C_{p_1} T \log T - k_1 T + b_1)}{RT},$$

and hence in the case of a reaction between ideal gases, K_p is a function of the temperature only. Thus we find

$$\frac{d \log K_p}{dT} = \frac{\sum \nu_1 (C_{p_1} T + b_1)}{RT^2} = \frac{-H_p}{RT^2}. \tag{18a}$$

Similarly the equilibrium constant K_c in terms of concentrations is defined as follows:

$$\log K_c = \sum \nu_1 \log c_1.$$

Now since $p_1 = c_1 RT$, $\log c_1 = \log p_1 - \log RT$ and

$$\log K_c = \log K_p - \sum \nu_1 \log RT. \tag{20}$$

Since K_p is a function of T only, the same is true of K_c, hence

$$\frac{d \log K_c}{dT} = \frac{d \log K_p}{dT} - \frac{\sum \nu_1}{T} = -\left(\frac{H_p + \sum \nu_1 RT}{RT^2}\right) = \frac{-H_v}{RT^2}, \tag{21}$$

where H_v is the loss in energy when the reaction takes place, usually termed the heat evolved at constant volume.

To summarize: when a reaction between ideal gases has reached equilibrium we have the following relations existing between the mole fractions, concentrations or partial pressures of the substances taking part in the reaction:

$$\left.\begin{aligned} \log K_x &= \sum \nu_1 \log x_1 \quad \text{or} \quad K_x = x_1^{\nu_1} x_2^{\nu_2} x_3^{\nu_3} \ldots, \\ \log K_c &= \sum \nu_1 \log c_1 \quad \text{or} \quad K_c = c_1^{\nu_1} c_2^{\nu_2} c_3^{\nu_3} \ldots, \\ \log K_p &= \sum \nu_1 \log p_1 \quad \text{or} \quad K_p = p_1^{\nu_1} p_2^{\nu_2} p_3^{\nu_3} \ldots \end{aligned}\right\} \quad (22)$$

Thus if the reaction considered is the union of hydrogen and oxygen to form water as given by equation (9), we shall have, if the subscripts 1, 2 and 3 refer respectively to hydrogen, oxygen and water,

$$K_x = \frac{x_3^2}{x_1^2 x_2}, \quad K_c = \frac{c_3^2}{c_1^2 c_2}, \quad K_p = \frac{p_3^2}{p_1^2 p_2}. \quad (23)$$

The set of equations (22) may be considered as the mathematical formulation of the Law of Mass Action for a reaction in gaseous systems, since these equations give the relation that holds between the concentrations of the various reacting substances at equilibrium. When the value of the equilibrium constant is known for a given temperature and pressure, we can predict with accuracy the effect produced in the system by varying the concentrations of the substances.

On account of the great importance of the law of mass action, it may be worth while to derive it in a somewhat different manner. We shall not, however, consider the most general case, but merely deduce the law for a particular case, viz.: the reaction given by equation (9). We suppose then that the volume V contains n_1 moles of H_2, n_2 moles of O_2 and n_3 moles of H_2O at the temperature T and the total pressure p. We desire to bring about the union of 2 moles of H_2 and 1 mole of oxygen to form 2 moles of H_2O in a thermodynamically reversible manner. We first imagine the three gases to be separated from each other so that we have n_1 moles of pure H_2 at the pressure p_1, n_2 moles of O_2 at the pressure p_2 and n_3 moles of water at the pressure p_3. The

temperature and volume of each gas are T and V. This separation can be brought about (see Chap. VIII and the discussion just preceding equation (4) of this chapter) without any change in the energy, entropy and thermodynamic potential of the gases. We shall also suppose that a certain vessel, which we may call the equilibrium box, contains the three gases at chemical equilibrium, their partial pressures in the equilibrium box being p_{1e}, p_{2e}, p_{3e}. The equilibrium box is supposed to have three semi-permeable walls, permeable respectively to H_2, O_2 and H_2O. We shall proceed to calculate the change in the total thermodynamic potential of the system when 2 moles of H_2 at the initial pressure p_1 and 1 mole of O_2 at the initial pressure p_2 are transformed reversibly and isothermally by means of the equilibrium box into 2 moles of H_2O at the pressure p_3. If Φ_1 is the thermodynamic potential of 1 mole of H_2, then $d\Phi_1 = -S_1\,dT + V_1\,dp_1 = -S_1\,dT + \dfrac{RT}{p_1}\,dp_1$; and if the hydrogen suffers a change in pressure at constant temperature then

$$d\Phi_1 = RT\,d\log p_1. \tag{24}$$

Similar expressions will hold for the oxygen and the water. Let us now expand 2 moles of hydrogen isothermally from p_1 to p_{1e} and 1 mole of oxygen from p_2 to p_{2e} and bring them in contact with the appropriate semi-permeable membranes. The total increase in thermodynamic potential so far will be

$$2\,RT\log\frac{p_{1e}}{p_1} + RT\log\frac{p_{2e}}{p_2}. \tag{25}$$

If we compress the two moles of H_2 and the one mole of oxygen into the equilibrium box and at the same time remove two moles of water vapor through the appropriate semi-permeable membrane at the pressure p_{3e}, the state of the equilibrium mixture will be absolutely unaffected and in particular the partial pressures of the various gases will have remained unchanged. This part of the process then (like the isothermal condensation of saturated vapor into liquid at the constant pressure of the saturated vapor) does not produce any change in the total thermodynamic

potential. Finally we transform isothermally the 2 moles of H_2O from the pressure p_{3e} to the pressure p_3, increasing its thermodynamic potential by the amount

$$2\,RT \log \frac{p_3}{p_{3e}}. \tag{26}$$

If now we denote by Φ_1 the total thermodynamic potential of our system in its original state and by Φ_2 the thermodynamic potential when two moles of hydrogen and one mole of oxygen have united to form two moles of water giving a final system at the same temperature and pressure, then the increase in the thermodynamic potential is as follows:

$$\Phi_2 - \Phi_1 = RT \log \frac{p_3^2}{p_1^2 p_2} - RT \log \frac{p_{3e}^2}{p_{1e}^2 p_{2e}}. \tag{27}$$

Now the change in the thermodynamic potential, like the change in the energy, entropy, free energy, etc., is a function of the initial and final states only (that is, in equation (27), $\Phi_2 - \Phi_1$ is a function of T and of p_1, p_2 and p_3) but is independent of the intermediate states through which the system has passed and therefore is independent of the particular partial pressures, p_{1e}, p_{2e}, p_{3e}, in the equilibrium box. At constant temperature and pressure then, the expression $RT \log \frac{p_{3e}^2}{p_{1e}^2 p_{2e}}$ must be a constant, which we can put equal to $RT \log K_p$, in agreement with our previous result. Rewriting equation (27) in the form

$$\Phi_1 - \Phi_2 = RT \log K_p - RT \log \frac{p_3^2}{p_1^2 p_2}, \tag{28}$$

we see that our system will be in chemical equilibrium if $\Phi_1 = \Phi_2$ (for in that case $\delta\Phi$ would be zero) and the condition that this shall be the case is

$$\log K_p = \log \frac{p_3^2}{p_1^2 p_2} \quad \text{or} \quad K_p = \frac{p_3^2}{p_1^2 p_2}. \tag{29}$$

Generalizing from these particular results, we see that if Φ_1 is the thermodynamic potential of a gaseous system and if Φ_2 is the thermodynamic potential of a system formed from the first one by a chemical change at constant temperature and pressure, then

$$\begin{aligned}(\Phi_1 - \Phi_2)_{T,\,p} &= RT \log K_p - RT \sum \nu_1 \log p_1 \\ &= RT \log K_c - RT \sum \nu_1 \log c_1 \\ &= RT \log K_x - RT \sum \nu_1 \log x_1, \end{aligned} \qquad (30)$$

where ν is negative if it refers to one of the initial substances and positive if it refers to one of the products.

Referring to Chap. IX and, in particular, to equations (20) and (21) of that chapter, we find that if $\Phi_1 - \Phi_2$ is positive, the reaction will proceed from the first state to the second; if $\Phi_1 - \Phi_2$ is zero, the substances are in chemical equilibrium and if $\Phi_1 - \Phi_2$ is negative, the reaction will proceed from the second state to the first. The function $(\Phi_1 - \Phi_2)$ is therefore a measure of the tendency of a chemical reaction to proceed in a given direction at constant temperature and pressure, and will accordingly be called the affinity of the reaction and represented by the symbol A or A_p.

Since the free-energy and thermodynamic potential are connected by the relation

$$\Phi = F + pV, \qquad (31)$$

it follows that the decrease in the free energy during an isothermal process at constant temperature and constant pressure is

$$\begin{aligned}(F_1 - F_2)_{T,\,p} &= (\Phi_1 - \Phi_2)_{T,\,p} + p\,(V_2 - V_1)_{T,\,p} \\ &= (\Phi_1 - \Phi_2)_{T,\,p} + \sum \nu_1 RT, \end{aligned} \qquad (32)$$

where V_1 and V_2 are the initial and final volumes at constant temperature and pressure. If the reaction takes place under these conditions without change in volume (this will occur if $\sum \nu_1 = 0$), then the decrease in free energy is equal to the decrease in the thermodynamic potential and hence equal to what we have designated the affinity of the process at constant temperature and pressure. But this equality holds only when the reaction occurs at constant pressure without change in volume. In general then we have

$$\left.\begin{aligned}(F_1 - F_2)_{T,\,p} &= RT \log K_p - RT \sum \nu_1 \log p_1 + \sum \nu_1 RT \\ &= RT \log K_c - RT \sum \nu_1 \log c_1 + \sum \nu_1 RT \\ &= RT \log K_x - RT \sum \nu_1 \log x_1 + \sum \nu_1 RT. \end{aligned}\right\} \qquad (33)$$

Reactions at Constant Temperature and Volume

According to equation (11) (Chap. IX) a system of substances will be in equilibrium at constant temperature and constant volume if any virtual infinitesimal process produces no change in the total free energy or in mathematical symbols if

$$\delta F = 0. \tag{34}$$

If F_1 represents the total free energy of equivalent quantities of the initial substances and F_2 that of equivalent quantities of the products of a reaction, then the system is in equilibrium at constant temperature and volume if

$$(F_1 - F_2)_{T,V} = 0. \tag{35}$$

Since at constant temperature, $dF = -p\,dV = V\,dp$ (for ideal gases) we can readily calculate the change in free energy when a reaction between ideal gases is carried out reversibly (for example, by means of an equilibrium box). If we have the final volume equal to the original volume, then the maximum work obtained (equal to the decrease in free energy) will be given by the following expression:

$$\left.\begin{aligned}(F_1 - F_2)_{T,V} &= RT \log K_p - RT \textstyle\sum \nu_1 \log p_1 \\ &= RT \log K_c - RT \textstyle\sum \nu_1 \log c_1 \\ &= RT \log K_x - RT \textstyle\sum \nu_1 \log x_1.\end{aligned}\right\} \tag{36}$$

The detailed deduction of the results in equation (36) may be left to the reader. From equation (31) it may easily be shown that, in general, for ideal gases,

$$(\Phi_1 - \Phi_2)_{T,V} = (F_1 - F_2)_{T,V} - \textstyle\sum \nu_1 RT. \tag{37}$$

If $(F_1 - F_2)_{T,V}$ is zero, the system is in equilibrium at constant temperature and volume. If it is positive, a chemical change will occur, increasing the quantity of the products; if it is negative, the reverse change will take place. We shall therefore call $(F_1 - F_2)_{T,V}$ the affinity of a process at constant temperature and volume and represent it by the symbol A_v.

The condition of equilibrium, $\delta F = 0$ or $(F_1 - F_2)_{T,V} = 0$, can most readily be applied in the case of reactions among gases

where it is a simple matter to maintain the volume constant. When reactions in which solids or liquids take part are under consideration, it is preferable to use the criterion $\delta\Phi = 0$ for equilibrium at constant temperature and pressure, although even in these cases, on account of the small volume changes, when the condition $\delta\Phi = 0$ is satisfied, the condition $\delta F = 0$ is also practically fulfilled.

Chemical Affinity

We shall not consider it necessary to dwell on the historical development of the ideas connected with the term "chemical affinity." From the point of view of atomistics, chemical affinity has to do with the various forces acting between the atoms and molecules of the substances concerned in a given chemical change. Our knowledge of these forces is at present too inaccurate and too incomplete for us to be able to attack the problem from this point of view. Thus if we have molecules of hydrogen, oxygen and water in a given space, there are doubtless forces between the various atoms in each kind of molecule, between the atoms in different molecules and between the various molecules. Some at least of these forces depend on the temperature which would for example determine the average distance apart of the atoms in a given kind of molecule. A complete knowledge of all these forces might enable one to predict the direction of chemical change and the final state of equilibrium, but evidently we are far from possessing such a detailed knowledge. Now, quite apart from all hypothetical views as to the atomic and molecular constitution of matter, we have deduced, on the basis of the two laws of thermodynamics, certain functions the values of which determine the direction of chemical changes and the state of equilibrium. Thus we found that for processes at constant temperature and pressure, the value of the function $A = (\Phi_1 - \Phi_2)_{T,\,p}$ and for isothermal processes at constant volume, the value of the function $A_v = (F_1 - F_2)_{T,\,V}$ determine the direction of any chemical change. We are therefore justified in considering these functions as quantitative measures of the chemical affinities which are active in any chemical change, even though the exact nature of these affinities

is unknown. It must be borne in mind that we shall not speak of the affinity of one substance for another, but of the affinity of a certain process. Thus we shall not speak of the affinity of hydrogen for oxygen but of the affinity of the process in which hydrogen and oxygen unite to form water, for the direction of the process depends not only on the concentrations of the hydrogen and of the oxygen but also on the concentration of the water vapor.

Our method of defining the affinity of a process is in its essentials due to van't Hoff. If a reaction is supposed to proceed isothermally at constant volume, the affinity of the process A_v is equal to the loss in free energy and therefore to the maximum work obtainable. For an isothermal process at constant pressure, the affinity A is equal to the decrease in the thermodynamic potential and therefore equal to the maximum work obtainable minus the purely mechanical work represented by the term $p\,(V_2 - V_1)$ where p is the constant pressure and V_1 and V_2 are the initial and final volumes.

Equilibrium Constant and Temperature

According to equation (30), we have

$$A = A_p = (\Phi_1 - \Phi_2)_{T,\,p} = RT \log K_p - RT \sum \nu_1 \log p_1. \qquad (38)$$

From this we easily deduce by differentiation,

$$\left(\frac{dA}{dT}\right)_p = \frac{A}{T} + RT \frac{d \log K_p}{dT}. \qquad (39)$$

Comparing (39) with equation (57) (Chap. IX) we obtain

$$\frac{d \log K_p}{dT} = -\frac{H_p}{RT^2}. \qquad (40)$$

Similarly from equation (36), we have

$$A_v = (F_1 - F_2)_{T,\,V} = RT \log K_c - RT \sum \nu_1 \log c_1,$$

and by differentiation at constant volume, since c_1, c_2, etc., remain constant,

$$\left(\frac{dA_v}{dT}\right)_v = \frac{A_v}{T} + RT \frac{d \log K_c}{dT}. \qquad (41)$$

Comparing (41) with equation (56) of Chap. IX, we obtain

$$\frac{d \log K_c}{dT} = -\frac{H_v}{RT^2}. \qquad (42)$$

It is usually advisable to use the equilibrium constants K_p or K_c rather than K_x, for the former are functions of the temperature only, whereas K_x is dependent on both temperature and pressure.

Equilibrium Constant and Heat of Reaction

From equation (40) or (42) we obtain on integration

$$\log K = \frac{H}{RT} - \int \frac{1}{RT} dH + \text{const.}$$

$$= \frac{H}{RT} - \int \frac{(C_1 - C_2)}{RT} dT + \text{const.}, \quad (43)$$

where C_1 is the heat capacity of the initial system and C_2 that of the products (see equation (33), Chap. VI). In equation (43), when the equilibrium constant is K_c, H stands for H_v and C_1 and C_2 for the heat capacities at constant volume; when the equilibrium constant is K_p, then H stands for H_p and C_1 and C_2 for the heat capacities at constant pressure. If K_1 and K_2 are the equilibrium constants at the absolute temperatures T_1 and T_2, then equation (43) becomes

$$\log \frac{K_2}{K_1} = \frac{H_2}{RT_2} - \frac{H_1}{RT_1} - \int_{T_1}^{T_2} \frac{C_1 - C_2}{RT} dT. \quad (44)$$

For the case in which H can be considered as constant over the temperature interval from T_1 to T_2 (and this means that $C_1 - C_2$ is zero or negligible) we have the following result:

$$\log \frac{K_2}{K_1} = \frac{H(T_1 - T_2)}{RT_1T_2}, \quad (45)$$

We can therefore express the heat of reaction according to (40) or (42) in the form

$$H = -RT^2 \frac{d \log K}{dT}, \quad (46)$$

or integrated in the form

$$H = \frac{RT_1T_2}{T_1 - T_2} \log_e \frac{K_2}{K_1}, (H = \text{constant}). \quad (47)$$

Expressing H in calories and using ordinary logarithms, we have

$$H_p = \frac{4.574\ T_1T_2}{T_1 - T_2} \log_{10} \frac{(K_p)_2}{(K_p)_1},$$
$$H_v = \frac{4.574\ T_1T_2}{T_1 - T_2} \log_{10} \frac{(K_c)_2}{(K_c)_1}. \qquad (48)$$

Dissociation of Hydrogen Iodide

Let us apply our formulas to the homogeneous gaseous reaction, $2\ HI \rightleftarrows H_2 + I_2$, studied by Lemoine,* and later by Bodenstein.† In this reaction, written in the form $-2HI + H_2 + I_2 = 0$, we see that $\sum \nu_1 = 0$ and hence according to equations (19) and (20) $K_x = K_c = K_p$. We shall therefore represent the equilibrium constant by K. K in this case is evidently a pure number, its value being independent of the units in which concentrations or partial pressures are expressed. In Tables XVI and XVII, the equilibrium concentrations of HI, H_2 and I_2 are expressed as cubic centimeters of the particular gas reduced to 0° C. and 760 mm. Since the reaction takes place isothermally without change in volume, the particular volume or pressure at which the reaction is investigated is without effect on the final state of equilibrium; the equilibrium constant is therefore given by the product of the quantities of H_2 and I_2 divided by the square of that of HI.

TABLE XVI. Temp. = 357° C.

I_2 in cc.	H_2 in cc.	HI in cc.	K	
0.10	4.14	4.98	0.0167	Average value of K = 0.01494 (Bodenstein)
0.93	1.44	9.55	0.0147	
4.46	0.47	11.88	0.0148	
19.95	0.14	12.54	0.0178	
17.73	0.13	12.17	0.0156	
15.93	0.15	12.71	0.0148	

* Ann. de chimie et de phys. [5], **12,** 145 (1877).

† Zeit. für phys. Chem., **13,** 56 (1893); **22,** 1 (1897); **29,** 295 (1899).

TABLE XVII. Temp. = 448° C.

I_2	H_2	HI	K	
0.12	5.28	5.64	0.0199	Average value of K = 0.01984 (Bodenstein)
0.55	3.19	9.49	0.0195	
2.53	1.33	13.47	0.0185	
6.97	0.65	14.93	0.0203	
19.76	0.25	15.54	0.0205	
25.40	0.19	15.40	0.0204	

The equilibrium state in reactions such as the foregoing is often described in terms of the fraction of the original substance or substances transformed. Thus if α represents the fraction of HI which has broken up into H_2 and I_2, α and K are connected in this case by the relation

$$K = \frac{\alpha^2}{4\,(1-\alpha)^2}. \tag{49}$$

The heat effect of the reaction $2\,HI \rightleftarrows H_2 + I_2$ can be calculated by means of equation (48), assuming that H is constant throughout the interval 357° C. to 448° C. We thus obtain

$$H = \frac{4.574 \times 630 \times 721}{-91} \log\left(\frac{0.01984}{0.01494}\right) = -2810 \text{ cal.}$$

Dissociation of Nitrogen Tetroxide

The equation for this reaction is $N_2O_4 \rightleftarrows 2\,NO_2$ or $-N_2O_4 + 2\,NO_2 = 0$, whence $\nu_1 = -1$ and $\nu_2 = 2$ and $\sum\nu_1 = 1$. If we suppose that we had originally one mole of N_2O_4 in V liters and if α is the fraction dissociated, then

$$K_c = \frac{\left(\frac{2\alpha}{V}\right)^2}{\frac{(1-\alpha)}{V}} = \frac{4\,\alpha^2}{(1-\alpha)V} = \frac{[NO_2]^2}{[N_2O_4]}.$$

If p_1 and p_2 are the partial pressures of N_2O_4 and NO_2 at equilibrium and if p is the total pressure, then evidently $pV = (1+\alpha)RT$; $p_1V = (1-\alpha)RT$; $p_2V = 2\,\alpha RT$. Hence the value of K_p is given by the expressions,

$$K_p = \frac{p_2^2}{p_1} = \frac{4\,\alpha^2 RT}{(1-\alpha)V} = K_cRT = \frac{4\,\alpha^2 p}{1-\alpha^2} \text{ (see equation (20)).}$$

The value of α can be calculated from determinations of the density of the equilibrium mixture. For if d_0 is the density which the gas would have if no dissociation had taken place and if d is the observed density, then

$$\frac{d_0}{d} = \frac{1+\alpha}{1} \quad \text{or} \quad \alpha = \frac{d_0 - d}{d}. \tag{50}$$

And in general if one molecule dissociates into n molecules

$$\frac{d_0}{d} = 1 + (n-1)\alpha \quad \text{or} \quad \alpha = \frac{d_0 - d}{(n-1)\,d}. \tag{51}$$

Applying equation (50) to the case of N_2O_4, we have

$$K_p = \frac{4\left(\frac{d_0 - d}{d}\right)^2 p}{1 - \left(\frac{d_0 - d}{d}\right)^2} = \frac{4(d_0 - d)^2 p}{d_0(2d - d_0)}. \tag{52}$$

Evidently, instead of the actual densities, we may let d_0 and d stand for the specific gravity with reference to any standard. In Table XVIII the numbers in the column headed d give the specific gravity compared with air at the same temperature and pressure. At 49.7° C., d_0 is evidently equal to the molecular weight of undissociated N_2O_4 divided by the (average) molecular weight of air, or $\frac{92.02}{28.95} = 3.179$. The value of K_p is expressed in atmospheres.

TABLE XVIII. $\begin{matrix} t = 49.7° \\ d_0 = 3.179 \end{matrix}$ $N_2O_4 \rightleftarrows 2\,NO_2$

p (mm.)	d (air = 1)	α	K_p (atmospheres)
93.75	1.788	0.777	0.752
182.69	1.894	0.678	0.818
497.75	2.144	0.483	0.797

If a molecule of a substance dissociates into two unlike molecules (as for example in the reaction $PCl_5 \rightleftarrows PCl_3 + Cl_2$) and if α is the degree of dissociation (it being assumed that one started with pure PCl_5), then in this case

$$K_c = \frac{[PCl_3] \times [Cl_2]}{[PCl_5]} = \frac{\alpha^2}{(1-\alpha)\,V} = \frac{\alpha^2 p}{(1-\alpha^2)\,RT}.$$

$$K_p = \frac{p_{PCl_3} \times p_{Cl_2}}{p_{PCl_5}} = \frac{\alpha^2 RT}{(1-\alpha)\,V} = \frac{\alpha^2 p}{1-\alpha^2}.$$

The formulas containing α can be used only when the quantities of PCl_3 and Cl_2 are equivalent, the others are perfectly general.

Dissociation of Water Vapor ($2\,H_2O \rightleftarrows 2\,H_2 + O_2$)

Confining our attention to the case in which the hydrogen and oxygen are present in chemically equivalent quantities and letting α equal the fraction of water dissociated, and p the total pressure, then

$$p_{H_2O} = \left(\frac{1-\alpha}{1+\frac{\alpha}{2}}\right)\cdot p; \quad p_{H_2} = \left(\frac{\alpha}{1+\frac{\alpha}{2}}\right)\cdot p,$$

$$p_{O_2} = \left(\frac{\frac{\alpha}{2}}{1+\frac{\alpha}{2}}\right)\cdot p \quad \text{and} \quad K_p = \frac{\alpha^3 p}{2\,(1-\alpha)^2\left(1+\frac{\alpha}{2}\right)}.$$

Since even at rather high temperatures α is small compared with unity, we may write $K_p = \frac{\alpha^3 p}{2}$. At any given temperature the degree of dissociation is therefore inversely proportional to the cube root of the total pressure. We shall return later to a study of this reaction.

Reactions in Heterogeneous Systems

If in addition to a gaseous phase, other phases of constant composition are present in the reacting system, the relations we have deduced are still applicable without appreciable change. Thus if a reaction is supposed to take place between various gases and a solid, we may imagine that the reaction in reality occurs between the gases and the vapor of the solid. The vapor pressure of the solid will be constant at all stages of the reaction. To fix our ideas, we may consider the reaction $NH_4HS \rightleftarrows NH_3 + H_2S$ where NH_4HS is a solid and at the temperature T has the vapor

pressure p_s. In any mixture let p_1 and p_2 be the partial pressures of NH_3 and H_2S respectively and in any equilibrium state let us represent the pressures by p_{1e}, p_{2e} and in the case of NH_4HS by p_s. In analogy with equation (27), the total increase in the thermodynamic potential when one mole of NH_4HS at the pressure p_s changes isothermally and at constant total pressure into one mole of NH_3 and one mole of H_2S is

$$\Phi_2 - \Phi_1 = RT \log \frac{p_1 p_2}{p_s} - RT \log \frac{p_{1e} p_{2e}}{p_s}, \qquad (53)$$

or the affinity of the process A at constant pressure is given by the following relation (since p_s cancels out).

$$A = \Phi_1 - \Phi_2 = RT \log K_p - RT \log (p_1 p_2), \qquad (54)$$

where $K_p = p_{1e} p_{2e} = p_{NH_3} \times p_{H_2S}$. We have therefore the following rule: if a solid (or liquid) of unchanging composition takes part in a gaseous reaction, the affinity A and the equilibrium constants K_p and K_c are calculated in the usual manner, taking only the gaseous substances into consideration. The student can easily convince himself that equation (30), viz.: $A = (\Phi_1 - \Phi_2)_{T,p} = RT \log K_p - RT \sum \nu_1 \log p_1$, will be unchanged if a solid is supposed to take part in the reaction, for if ν_s is the number of moles of the solid which react and if p_s is the vapor pressure of the solid, the quantity $\nu_s \log p_s$ will be added to $\log K_p$ and also to $\sum \nu_1 \log p_1$ and the value of A will be unaltered.

Examples of Heterogeneous Reactions

As the simplest example of a heterogeneous reaction, we may take the equilibrium between a solid or liquid and the vapor of the substance. Consider for example the equation, H_2O (liquid) $\rightleftarrows H_2O$ (gas). If p_s is the pressure of water vapor in equilibrium with liquid water at the temperature T, we have

$$K_p = p_s; \quad A = RT \log K_p - RT \log p$$

or

$$A = RT \log p_s - RT \log p,$$

if p is the pressure of water vapor. We see that A is positive if $p < p_s$, zero if $p = p_s$ and negative if $p > p_s$ and from these re-

sults we can predict whether in any given case water will vaporize or water vapor condense.

According to equation (40),

$$\frac{d \log K_p}{dT} = \frac{d \log p_s}{dT} = -\frac{H_p}{RT^2},$$

and since $-H_p = L$ (the latent heat of vaporization) we have

$$L = RT^2 \frac{d \log p_s}{dT},$$

the form which the Clausius-Clapeyron equation takes when we assume water vapor to be an ideal gas and neglect the volume of the liquid, (see equation (31), Chap. X).

Formation of Hydrated Salts

We shall take as a typical example the process represented by the equation

$$CuSO_4 \cdot 3\,H_2O + 2\,H_2O \rightleftarrows CuSO_4 \cdot 5\,H_2O.$$

If p_e is the pressure of the water vapor at equilibrium, then $K_p = \frac{1}{p_e^2}$. If in a certain vessel we have the two hydrated salts and either ice or water (the water not in contact with the salts) and if the vapor pressure of the ice or pure water be represented by p_0, then the affinity of the reaction represented by the above equation (since $\sum \nu_1 = -2$) is

$$A = RT \log K_p - RT \sum \nu_1 \log p_1 = RT \log \frac{1}{p_e^2} + RT \log p_0^2.$$

The heat of the reaction H_p is

$$H_p = -RT^2 \frac{d \log K_p}{dT} = -RT^2 \frac{d \log \frac{1}{p_e^2}}{dT} = 2\,RT \frac{d \log p_e}{dT}.$$

If we refer all quantities to a reaction in which one mole only of water or of ice reacts, then

$$A = RT \log \frac{p_0}{p_e} \quad \text{and} \quad H_p = RT \frac{d \log p_e}{dT}. \tag{55}$$

In Table XIX are given the affinities and heats of reaction in processes in which one mole of ice reacts with a salt at 0° C. The calculations are due to Schottky.* The values of H_p are derived from Thomsen's thermochemical data.

TABLE XIX. Ice + Salt at 0° C.

Reaction	H_p per mole of ice in calories	A per mole of ice in calories
$CuSO_4 \cdot 3\,H_2O + 2\,H_2O$	1190	840
$ZnSO_4 \cdot H_2O + 5\,H_2O$	554	480
$MnSO_4 \cdot H_2O + 4\,H_2O$	336	359
$FeSO_4 \cdot H_2O + H_2O$	200	275
$CuSO_4 + H_2O$	4860	2350

Dissociation of Limestone, $CaCO_3 \rightleftarrows CaO + CO_2$

If p_e is the pressure of CO_2 in equilibrium with $CaCO_3$ and CaO, then $K_p = p_e$ and H_p, the heat evolved in the dissociation of one mole of $CaCO_3$, is given by equation (48). In Table XX we give the dissociation pressures of $CaCO_3$ as measured by Johnston † and the values of H_p calculated by means of equation (48).

TABLE XX. $CaCO_3 \rightleftarrows CaO + CO_2$

$t°$	T	p (mm. Hg)	$-H_p$ (calc.)	$-H_p$ (observed)
671	944	13.5	.....	43,000 cal. at ordinary temperature (Thomsen)
711	984	32.7	40,800	
748	1021	70.0	41,100	
819	1092	235.0	37,800	
894	1167	716.0	37,600	

Evidently the affinity of this reaction is given by the equation $A = RT \log \frac{p_e}{p}$ if p is the initial pressure of CO_2. If p is greater than p_e, the affinity is negative and therefore CO_2 will combine with CaO to form $CaCO_3$.

Let us finally consider the homogeneous gaseous reaction $H_2 + CO_2 \rightleftarrows H_2O + CO$. In this case since $\sum \nu_1 = 0$, $K_x = K_c$

* Zeit. f. phys. Chem. **64**, 422 (1908).

† J. Amer. Chem. Soc., **32**, 938 (1910).

$= K_p = K$. At 886° C., the value of K is 1.197. What will happen if we mix one mole of each of the four substances at 886° C.? Evidently no matter what the total volume or pressure may be, $\sum \nu_1 \log p_1$ is equal to zero, and therefore we have

$$A = RT \log K = RT \log_e 1.197 = 414 \text{ cal.}$$

Since A is positive, the reaction will proceed, as written, from left to right until equilibrium is reached.

Law of Mass Action for Dilute Solutions

According to equation (8) of Chap. XIII, the total thermodynamic potential of a dilute solution containing N_0 moles of solvent, and N_1, N_2 . . . moles of various solutes is given by the expression

$$\Phi = N_0 (\Phi_0)_0 + N_1 (\Phi_1)_0 + N_2 (\Phi_2)_0 + \cdots + RT (N_0 \log x_0 + N_1 \log x_1 + N_2 \log x_2 + \cdots), \quad (56)$$

in which x_0, x_1, x_2 are the respective mole fractions and $(\Phi_0)_0$ is the thermodynamic potential of one mole of pure solvent. As regards $(\Phi_1)_0$ and $(\Phi_2)_0$, all we need to bear in mind is that they refer to the solutes and are functions of T and the total pressure p only. Our general condition of equilibrium is that for any infinitesimal virtual variation during which the temperature and pressure are maintained constant, $\delta\Phi$ must equal zero. Let the infinitesimal variation consist in the chemical change in which the mole numbers suffer the variations δN_0, δN_1, δN_2, etc., these being proportional to the finite quantities, ν_0, ν_1, ν_2, the molecular coefficients in the stoichiometric equation of the reaction. In this variation $(\Phi_0)_0$, $(\Phi_1)_0$, etc., remain unvaried, since T and p are kept constant. We therefore obtain

$$\delta\Phi = \delta N_0 \cdot (\Phi_0)_0 + \delta N_1 \cdot (\Phi_1)_0 + \cdots + RT [\delta N_0 \cdot \log x_0 + \delta N_1 \log x_1 + \cdots] + RT \left[N_0 \cdot \frac{\delta x_0}{x_0} + N_1 \frac{\delta x_1}{x_1} + \cdots \right] = 0. \quad (57)$$

The term

$$\frac{N_0}{x_0} \delta x_0 + \frac{N_1}{x_1} \delta x_1 + \cdots = (N_0 + N_1 + N_2 + \cdots)(\delta x_0 + \delta x_1 + \delta x_2 \cdots)$$

and since $x_0 + x_1 + x_2 + \cdots = 1 =$ a constant, the said term is equal to zero. We therefore obtain as a condition of equilibrium

$$\delta N_0 \cdot \log x_0 + \delta N_1 \cdot \log x_1 + \cdots = -\frac{\delta N_0 (\phi_0)_0 + \delta N_1 (\phi_1)_0 + \cdots}{RT}. \quad (58)$$

Substituting for δN_0, δN_1, δN_2, the finite quantities ν_1, ν_2, ν_3, which are proportional to them, we have

$$\sum \nu_0 \log x_0 = -\frac{\sum \nu_0 (\phi_0)_0}{RT} = f(T, p). \quad (59)$$

At constant temperature and pressure, $\sum \nu_0 \log x_0$ is a constant when equilibrium obtains. We can therefore write

$$\sum \nu_0 \log x_0 = \log K_x = -\frac{\sum \nu_0 (\phi_0)_0}{RT} = f(T, p). \quad (60)$$

We thus obtain for the equilibrium constant K_x for a reaction in dilute solutions, exactly the same equation as for a reaction between ideal gases (see equation (13)). If the solvent does not take part in the reaction, ν_0 is zero and the expression for the equilibrium constant becomes

$$\log K_x = \sum \nu_1 \log x_1, \quad (61)$$

where $\sum \nu_1 \log x_1$ refers only to the solutes. Even if the solvent does take part in the reaction, the value of x_0 will be so close to unity in dilute solutions that $\nu_0 \log x_0$ may be taken as zero and hence, in this case also, equation (61) will be applicable.

Since in dilute solutions, reactions produce negligible changes of volume and since alterations in the total pressure also bring about inappreciable volume changes, we may consider the total volume of the solution as a constant. Hence if we set $\log K_c = \sum \nu_1 \log c_1$ where c_1, c_2, etc., are the equilibrium concentrations, we obtain, since

$$c_1 = \frac{N_1}{V} = x_1 \frac{(N_0 + N_1 + N_2 + \cdots)}{V},$$

$$\log K_c = \log K_x + \sum \nu_1 \log \frac{N_0 + N_1 + N_2 + \cdots}{V}. \quad (62)$$

But since in dilute solutions, $N_1 + N_2 + \cdots$ is small compared with N_0, the last term in (62) may be considered as constant, and hence, since $\log K_x$ is constant, so also is $\log K_c$. The law of mass action as applied to gaseous reactions holds therefore for reactions in dilute solutions whether we deal with mole fractions or concentrations of the reacting substances.

According to equation (30) of Chap. XIII, we can attribute to a substance, N_1 moles of which are present in a dilute solution the total volume of which is V, an osmotic pressure P_1, given by the relation

$$P_1V = N_1RT \quad \text{or} \quad P_1 = C_1RT. \tag{63}$$

Accordingly if we define $\log K_p$ as equal to $\sum \nu_1 \log P_1$, where $P_1, P_2 \ldots$ are the osmotic pressures of the reacting substances at equilibrium, then

$$\log K_p = \sum \nu_1 \log C_1 + \sum \nu_1 RT = \log K_c + \sum \nu_1 RT \tag{64}$$

and therefore K_p is a constant at constant temperature.

On account of the importance of the subject, it may not be out of place to consider the whole matter of equilibrium in dilute solutions from a somewhat different point of view. Let us suppose that we have a dilute solution consisting of N_0 moles of water and N_1 moles of sugar at the temperature T. Let V be the volume of the solution containing N_1 moles of sugar; then if the solution is sufficiently dilute, equation (63) holds. Let us suppose that the volume V of the solution is separated by means of a semi-permeable piston from pure water. Thus in Fig. 53,

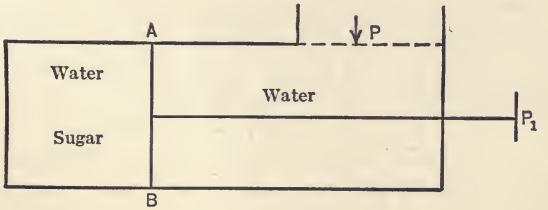


FIG. 53

the osmotic pressure on the piston AB is balanced by the pressure P_1. The pressure on the water is p (ordinarily one atmosphere). In this system we can say that the water is under the pressure p

and the sugar is under the pressure P_1. The thermodynamic potential of one mole of sugar in the solution is $U_1 - TS_1 + P_1V_1$ where V_1 is the volume of solution containing one mole of sugar. We therefore see that the thermodynamic potential of a substance in very dilute solution is given by an expression identical with that for an ideal gas if we substitute osmotic pressure for the partial pressure of the gas. Since a dilute solution is characterized by the fact that further dilution produces no heat effect, the energy U_1 of a mole of solute in dilute solution is independent of the volume or osmotic pressure; that is U_1 is a function of the temperature only. If the piston AB moves reversibly to the right, increasing the volume of solution by dV, the work W done on the surroundings is $W = P_1\,dV$. Hence Q, the heat absorbed, will be $Q = N_1\,dU_1 + P_1\,dV = N_1T\,dS_1$. In other words

$$dS_1 = \frac{dU_1 + \frac{P_1}{N_1}\,dV}{T} = \frac{dU_1}{T} + R\frac{dV}{V} = \frac{dU_1}{T} + R\frac{dV_1}{V_1}\cdot$$

If the specific heat of the dissolved substance is C_{v_1}, then $dU_1 = C_{v_1}\,dT$ and $dS_1 = C_{v_1}\frac{dT}{T} + \frac{R}{V_1}\,dV_1$. We accordingly see that the expressions for the energy, entropy, and thermodynamic potential of a substance in dilute solution are identical with those found for ideal gases, the only change being the substitution of the osmotic pressure for the partial pressure of the gas. We can therefore apply to reactions in dilute solutions the important relations dealing with the equilibrium constant, the affinity, the heat of reaction, etc., as expressed in equations (30), (40), (42), (48), etc. Since reactions in dilute solution take place at practically constant volume, the heat of the reaction as ordinarily measured is represented by H_v. H_p has been defined as the heat of a reaction at constant pressure, but when equation (40) is applied to reactions in dilute solution, H_p denotes the heat evolved at constant total osmotic pressure. In other words, the equation $H_p = H_v - \sum\nu_1RT$ holds for reactions in dilute solutions as well as for reactions in gaseous systems. Examples of chemical equilibrium in solutions will be given in the next chapter.

PROBLEMS

1. At 448° C., the degree of dissociation of HI is 0.2198. Calculate K_c and K_p. If previous to dissociation, the system contained 1 mole of HI at 1 atmosphere, and if the pressure is kept constant, calculate the partial pressures of HI, H_2 and I_2 at equilibrium.

2. If 0.05 mole of HI, 0.02 mole of I_2 and 0.01 mole of H_2 are brought together at 357° C. into a total space of 4 liters, calculate the composition of the equilibrium mixture in moles, mole fractions, concentrations and partial pressures, assuming $K_c = 0.01494$ (Bodenstein).

3. If 0.05 mole of H_2 and 0.01 mole of I_2 are brought together at 448° C. what fraction of the original iodine will exist as HI? (Use equilibrium constant from problem 1.)

4. PCl_5 dissociates according to the equation $PCl_5 \rightleftarrows PCl_3 + Cl_2$. The degree of dissociation at atmospheric pressure is 0.485 at 200° C. and 0.800 at 250° C. Calculate the mole fractions, concentrations, and partial pressures at equilibrium and the values of K_x, K_c and K_p at each temperature.

5. From the data in problem 4, calculate the heat of dissociation of PCl_5 at constant volume and at constant pressure, over the temperature range 200°–250° C.

6. Solid ammonium hydrosulphide dissociates according to the equation $NH_4HS \rightleftarrows NH_3 + H_2S$, and the vapor phase contains practically no solid NH_4HS. At 10.1° C. and at 25.1° C., the dissociation pressures are 184 and 501 mm. respectively. Calculate K_c and K_p at each temperature. Calculate the heat of sublimation of 1 mole of NH_4HS at constant pressure at an average temperature of 17.6° C. Calculate the change in energy accompanying the sublimation.

7. Into a liter vessel at 25.1° C. are put 0.05 mole of NH_3 and 0.04 mole of H_2S. What will be the final partial pressures, the total pressure and what amount of solid NH_4HS will be formed? (Find K_p from problem 6.)

8. If K_1 and K_2 are the equilibrium constants at the temperature T for the two reactions $2\ CO_2 \rightleftarrows 2\ CO + O_2$ and $2\ H_2O \rightleftarrows 2\ H_2 + O_2$ respectively, find the value of K_3, the equilibrium constant at the temperature T for the reaction $H_2 + CO_2 \rightleftarrows H_2O + CO$.

9. For the reaction $2\ SO_3 \rightleftarrows 2\ SO_2 + O_2$, the values of K_c at a number of temperatures are: 627° C., 0.000316; 727° C., 0.00354; 832° C., 0.0280. Calculate the values of K_p for each temperature. Also calculate the heat of the reaction for the intervals 627°–727° and 727°–832°.

10. From the data in problem 9 calculate the values of K_c and K_p at the temperatures, 500° C. and 1000° C. What fraction of SO_3 will be dissociated at each of the temperatures, 500, 627, 727, 832 and 1000° C., the total pressure being 1 atmosphere?

11. Assuming air to be 79 per cent N_2 and 21 per cent O_2 by volume, what per cent of SO_2 will be transformed into SO_3 if equal volumes of SO_2 and air are mixed at 627° C. under a total pressure of 1 atmosphere? (See problem 9.)

12. At 21.5° C. and a pressure of 59 7 mm., the degree of dissociation of N_2O_4 is 0.483. Find K_c and K_p. Calculate the volume occupied by one (original) mole of N_2O_4. At what pressure will the degree of dissociation be 0.1?

13. A mixture containing 49 per cent of HCl and 51 per cent O_2 by volume was heated at a constant pressure of 723 mm. to 480° C. At equilibrium 76 per cent of the HCl had been transformed according to the equation $4\,HCl + O_2 \rightleftarrows 2\,Cl_2 + 2\,H_2O$. Find the values of K_c and K_p (pressures in atmospheres).

14. Calculate the composition of the equilibrium mixture obtained at 480° C. and 720 mm., starting with a mixture which is 25 per cent HCl and 75 per cent O_2 by volume (see problem 13).

15. If CO_2 at 1000° and 1 atmosphere, is dissociated to the extent of 0.003 per cent, find the value of K_p.

16. If oxygen is passed through carbon at 1000°, we shall have present, C, CO, and CO_2 and a small amount of oxygen. If at a total pressure of 1 atmosphere, the gaseous mixture is 99.3 per cent CO and 0.7 per cent CO_2, find the partial pressure of the oxygen present. Determine also the equilibrium constant of the reaction $C + CO_2 \rightleftarrows 2\,CO$ (see problem 15). *Ans.* $p_{O_2} = 6.71 \times 10^{-19}$ atmosphere.

17. From the data of problem 16 calculate the composition at 1000° C. and a total pressure of 1 atmosphere, of the gaseous mixture obtained by a reaction between carbon and air, if the equilibrium mixture is 60 per cent nitrogen by volume.

18. From the data of problems 15 and 16 determine K_p at 1000° C. for the reaction $C + O_2 \rightleftarrows 2\,CO$.

19. From the data of problems 15 and 16, calculate the affinity of the process in which 1 mole of oxygen at 1 atmosphere and 1000° C. is isothermally combined with carbon to form CO_2 at 1 atmosphere.

20. From problems 15, 16 and 18, determine the affinity of the process in which 1 mole of oxygen at 1 atmosphere and 1000° C. is isothermally combined with carbon to form CO at 1 atmosphere.

21. Assuming the following reaction, $Fe_3O_4 + 4\,H_2 \rightleftarrows 3\,Fe + 4\,H_2O$, at 900° C., we have $p_{H_2} = 71.8$ mm., and $p_{H_2O} = 49.3$ mm. Calculate the value of K_p at 900° C.

22. The equilibrium constants of the reaction in problem 21 are as follows: at 727° C. $(0.57)^4$; at 1025° C., $(0.78)^4$; at 1150° C., $(0.86)^4$. Calculate from these data and from problem 21, the heat of the reaction for three different temperature intervals.

CHAPTER XVI

CHEMICAL EQUILIBRIUM IN LIQUID SOLUTIONS

In Chap. XV it was shown that the laws and relations that hold for gaseous systems can be applied to reactions in dilute solutions, if we substitute osmotic pressures for partial gaseous pressures. We shall consider first a reaction studied by Cundal,* viz., the dissociation of N_2O_4 in various solvents, such as chloroform, benzene, methylene chloride, etc. The results in Table XXI are taken from calculations by Ostwald † based on the experimental work of Cundal.

TABLE XXI. N_2O_4 IN CHLOROFORM AT 0° C.

$V \frac{\text{liters}}{\text{mole}}$	α = degree of dissociation	$K = \frac{4\alpha^2}{(1-\alpha)V}$
4.28	0.00239	5.36×10^{-6}
2.06	0.00152	4.48×10^{-6}
1.54	0.00145	5.44×10^{-6}
1.16	0.00140	6.76×10^{-6}
0.87	0.00115	6.04×10^{-6}

The values of K in the third column vary irregularly, due doubtless to experimental error and the fact that the solutions investigated were not very dilute.

In this connection we may discuss the relation that exists between the equilibrium in a gaseous system and the equilibrium between the same substances in a liquid phase. For let us imagine that above the chloroform we have a gas phase containing N_2O_4 and NO_2. Let c_1 and c_2 be the concentrations of N_2O_4 and NO_2 respectively in the gas phase, and C_1 and C_2 their concentrations in the liquid phase at equilibrium. Assuming Henry's law, $C_1 = a_1c_1$ and $C_2 = a_2c_2$. If K' is the equilibrium constant for the gaseous reaction, $K' = \frac{c_2^2}{c_1}$ and similarly K (the equi-

* Jour. Chem. Soc., 1891, p. 1076, and 1895, p. 794.

† Allgem. Chemie. Verwandschaftslehre, p. 600.

librium constant for the reaction in the liquid) is equal to $\frac{C_2^2}{C_1}$.

Hence $$K = \frac{a_2^2}{a_1} \cdot K'.$$

The equilibrium constant for a reaction in dilute solution can therefore be calculated from the equilibrium constant for the same reaction in a gaseous system if the solubilities of the various gases in the liquid are known. Evidently also the equilibrium constants for a reaction in two different liquid media can be calculated in the same manner; and if the two media are immiscible, the value of K in one liquid can be calculated from the value of K in the second medium, if the distribution or partition coefficients are known.

Dissociation in Solution

In the study of the properties of gases, it was found that the behavior of certain substances could be accounted for on the hypothesis that dissociation had taken place to a certain extent. Thus the properties of the gas of the empirical formula NO_2 can be accounted for on the assumption that the gas contains two molecular species, N_2O_4 and NO_2. Applying the laws of thermodynamics to the system, we find that we obtain results in harmony with the facts; in particular, if we know the density of the gas at a given temperature and pressure, we can calculate the density at the same temperature and at any other pressure. In such cases as the systems, N_2O_4, PCl_5, NH_4Cl, etc., the experimental evidence that dissociation occurs is very strong. The formulation of the dissociation by means of such an equation as $N_2O_4 \rightleftarrows 2\ NO_2$ is of course based on the atomic and molecular theories and is therefore as hypothetical as these theories. The general agreement between the facts and the results predicted on the basis of theory proves the great value of the theories, if not their ultimate truth. We are therefore justified in applying the laws of thermodynamics to chemical reactions considered from the standpoint of atomistics and this we have already done in many instances.

In the case of aqueous solutions of acids, bases and salts, the experimental evidence derived from the behavior of the solutions has led to the supposition that in these solutions the dissolved substances are dissociated to a greater or less extent into what are called ions. (Arrhenius, 1887.) Investigation since 1887 has shown the great value of the theory of ionization and in our study of the equilibria between salts in solutions, we shall make use of this theory of ionization in the interpretation of our results.

Equilibrium between Solid and Solution

In Chap. XI we discussed the equilibrium between a solid and a solution from the purely thermodynamic standpoint. We shall now consider the same subject, introducing the hypotheses that the solution is so dilute that van't Hoff's laws of osmotic pressure apply and that the dissociation in solution is negligible. Let T, P, C be the temperature, osmotic pressure and concentration of a solution in equilibrium with a solid. We represent the process that may take place by the equation

$$\text{Solid} \rightleftarrows \text{solution}. \qquad (1)$$

For this equilibrium at a given temperature and pressure, we shall have

$$K_c = C, \qquad K_p = P = CRT. \qquad (2)$$

According to equation (43), Chap. XIII, the osmotic pressure of a solution is to a great extent independent of the external pressure; hence we may, as in the case of gaseous systems, consider K_c and K_p as functions of the temperature only. Representing by H_s the heat of the reaction according to equation (1), we have (see equation (42), Chap. XV)

$$H_s = -RT^2 \frac{d \log K_c}{dT} = -RT^2 \frac{d \log C}{dT}, \qquad (3)$$

where H_s is the heat evolved when one mole of the solid dissolves in the saturated solution. By hypothesis, the saturated solution is also a dilute solution and hence H_s should not differ appreciably from the heat evolved when one mole of the solid dissolves in the pure solvent to form a saturated solution. Equation (3) can be deduced from equation (38), Chap. XI. According to the

latter the heat evolved when one mole of *solvent* unites with a solid to form a saturated solution is $RT^2 \frac{d \log \frac{p}{p_0}}{dT}$ where p_0 is the vapor pressure of the pure solvent and p that of the saturated solution. If the concentration of the saturated solution is C and if V_0 is the molecular volume of the liquid solvent, then in the saturated but dilute solution, we have one mole of solvent to CV_0 moles of solute. Hence the heat evolved when one mole of *solid* combines with the water to form a saturated solution is equal to

$$\frac{1}{CV_0} \cdot RT^2 \frac{d \log \frac{p}{p_0}}{dT}.$$

Now from equation (27), Chap. XIII,

$$\log_e \frac{p}{p_0} = -\frac{PV_0}{RT} = -CV_0.$$

Hence it is easily seen, since

$$d \log_e \frac{p}{p_0} = -V_0 \, dC,$$

that the heat evolved is equal to

$$-RT^2 \frac{d \log C}{dT},$$

in agreement with equation (3). Strictly speaking, H_s of equation (3) is called the differential heat of solution or the heat evolved when one mole of solid dissolves in a very large quantity of the saturated solution. To be distinguished from this is the integral heat of solution, obtained when one mole of solid dissolves in enough solvent to form a saturated solution; and finally there is what is usually called the "heat of solution," the heat evolved when one mole of solid is dissolved in a very large amount of solvent. In the case of sparingly soluble solids, the three kinds of heat of solution may be regarded as equal.

Solubility of Succinic Acid in Water

The solubility of succinic acid is 2.35 grams at 0° C. and 6.76 grams at 24.8° C. in 100 grams of water. Equation (3) integrated on the assumption that H_s is constant becomes

$$H_s = \frac{4.574\ T_1T_2}{T_1 - T_2} \log_0 \frac{C_2}{C_1} \tag{4}$$

Applying this equation to the case of succinic acid and water, we may take $\frac{C_2}{C_1}$ equal to the ratio of 6.76 to 2.35 and thus obtain $H_s = -6880$. Berthelot found for the heat of dilute solution -6700 calories. We have assumed that the dissociation of succinic acid is negligible and that the differential heat of solution is essentially the same as the heat of dilute solution.

Ionic Equilibrium

According to the theory of ionization, when a binary electrolyte is dissolved in water, we have an equilibrium which may be represented as follows (taking an acid of the general formula HA as an example):

$$HA \rightleftarrows \overset{+}{H} + \overset{-}{A} \tag{5}$$

Assuming the solution to be dilute, we shall have

$$K_c = \frac{[\overset{+}{H}] \times [\overset{-}{A}]}{[HA]}. \tag{6}$$

If we assume the solution to contain one (original) mole of the acid in V liters of solution and if α is the degree of dissociation, we readily obtain, since $C = \frac{1}{V}$,

$$K_c = \frac{\alpha^2}{(1 - \alpha)\ V} = \frac{C\alpha^2}{1 - \alpha}, \tag{7}$$

where K_c is called the dissociation constant. Equation (7) is sometimes called Ostwald's dilution formula, so named because it gives the relation between the degree of dissociation α and the dilution, V. An application of equation (7) to the dissociation of acetic acid is given in Table XXII. The method used in calculating α will be discussed later.

TABLE XXII. ACETIC ACID AT 25° C.

V liters per mole	$\alpha \times 100$	$K = \frac{\alpha^2}{(1-\alpha)V}$
8	1.193	0.0000180
16	1.673	0.0000179
32	2.380	0.0000182
64	3.33	0.0000179
128	4.68	0.0000179
256	6.56	0.0000180
512	9.14	0.0000180
1024	12.66	0.0000177

Similar results have been obtained for all the so-called weak acids and weak bases. In the case of salts and the strong acids and bases, equation (7) no longer holds. Now solutions of salts, strong acids or strong bases differ from those of weak acids or weak bases in having a relatively high ionic concentration. Attempts have been made to show how this circumstance would cause the dissolved substances to depart widely in their behavior from that characteristic of solutions of weak electrolytes. Moreover even the methods of calculating the degree of dissociation of electrolytes are more or less uncertain. We shall return to this matter later. For the present we shall bear in mind that the law of mass action as expressed in equation (7) holds with considerable accuracy for solutions of weak acids and weak bases but is no longer valid for solutions of strong electrolytes. In the latter case it may be used as an approximate formulation for small changes in concentration and as a fairly exact guide if the solution is exceedingly dilute; for example, in dealing with solutions of highly insoluble salts (AgCl, $CaSO_4$, etc.).

Activity

In this connection we may introduce a term which has proved to be convenient in expressing how far substances depart from the behavior characteristic of ideal gases or of solutes in an ideal dilute solution. For one mole of an ideal gas we have, if Φ_1 and Φ_2 are the thermodynamic potentials at the pressures p_1 and p_2 or concentrations c_1 and c_2 (the temperature remaining unchanged),

$$\Phi_2 - \Phi_1 = RT \log_e \frac{p_2}{p_1} = RT \log_e \frac{c_2}{c_1}. \qquad (8)$$

Equation (8) holds for substances in ideal dilute solution if we substitute the osmotic pressures P_1 and P_2 for the gas pressures p_1 and p_2. For actual substances, whether gases or in solution, equation (8) is no longer exact. We shall define the activities of a substance in two different states at the same temperature, firstly, by the equation

$$\Phi_2 - \Phi_1 = RT \log_e \frac{a_2}{a_1}, \tag{9}$$

and secondly, by the statement that as the concentration approaches zero, the activity becomes identical with the concentration. We make the fundamental assumption that at infinite dilution every substance exhibits ideal behavior. In practice, it is possible to set the activity as essentially equal to the concentration at small but finite concentrations. Further discussion of this point must be reserved for a later chapter, but it may be pointed out here that the law of mass action will hold exactly if we substitute activities for concentrations in the expression for K_c.

We have previously calculated the heat of solution of succinic acid in water from the solubilities at two temperatures, assuming the degree of dissociation to be negligible. We shall now discuss the case in which appreciable dissociation occurs, first however considering the analogous case of the evaporation of a liquid or solid which suffers dissociation in the gaseous phase. To take a particular case, let us imagine liquid N_2O_4 in equilibrium with the vapor phase, consisting of a mixture of N_2O_4 and NO_2. If p is the total pressure of the gas, T the temperature, v_1 and v_2 the volumes of one gram of the liquid and gaseous phases respectively and λ is the heat absorbed when one gram of liquid N_2O_4 is vaporized at constant pressure p and temperature T, then, applying the Clapeyron-Clausius formula, we have

$$\lambda = T(v_2 - v_1)\frac{dp}{dT}. \tag{10}$$

If M is the molecular weight corresponding to the formula N_2O_4, and if α is the degree of dissociation of the gas mixture, then

$$v_2 = \frac{(1 + \alpha)RT}{pM}. \tag{11}$$

Substituting in equation (10), neglecting v_1 in comparison with v_2 and representing by $L = M\lambda$, the latent heat of evaporation of one mole of N_2O_4, we obtain

$$L = (1 + \alpha) RT^2 \frac{d \log p}{dT} = iRT^2 \frac{d \log p}{dT}. \qquad (12)$$

If we represent by C, the analytical concentration of N_2O_4 in the gas phase (that is, if W is the weight and V is the volume of the gas and if M is the molecular weight of N_2O_4, $C = \frac{W}{MV}$), then we have (setting $i = 1 + \alpha$)

$$p = (1 + \alpha) CRT = iCRT. \qquad (13)$$

From (13),

$$\frac{d \log p}{dT} = \frac{d \log (iC)}{dT} + \frac{1}{T},$$

and hence from (12)

$$L - iRT = iRT^2 \frac{d \log (iC)}{dT}. \qquad (14)$$

Since iRT represents the external work, $L - iRT$ represents the change in energy during the evaporation of one mole of liquid N_2O_4 or the internal latent heat of vaporization. This evaporation gives rise to $i = 1 + \alpha$ moles of the gas mixture, in which the actual total concentration on account of dissociation is iC, where C is the concentration calculated on the assumption that the gas is wholly N_2O_4. The actual concentration of undissociated N_2O_4 in the gas will be $(1 - \alpha) C$, and that of NO_2 will be $2\alpha C$, whence

$$K_c = \frac{4 \alpha^2 C}{1 - \alpha}.$$

Since $\alpha = i - 1$, we have

$$K_c = \frac{4 (i - 1)^2 C}{(2 - i)}. \qquad (15)$$

If we let H_v be the heat of dissociation of N_2O_4 at constant volume, then

$$H_v = -RT^2 \frac{d \log K_c}{dT}. \qquad (16)$$

From equation (15), we deduce

$$\frac{d \log K_c}{dT} = \frac{d \log C}{dT} + \frac{3 - i}{(i - 1)(2 - i)} \cdot \frac{di}{dT} = -\frac{H_v}{RT^2}. \qquad (17)$$

Now equation (14) may be written in the form

$$L - iRT = iRT^2 \frac{d \log C}{dT} + RT^2 \frac{di}{dT}. \qquad (14a)$$

Substituting in (14a) the value of $\frac{di}{dT}$ from (17) we obtain

$$L - iRT = \frac{2}{3 - i} \cdot RT^2 \frac{d \log C}{dT} - \frac{(i - 1)(2 - i)}{(3 - i)} H_v. \qquad (18)$$

When $i = 1$, that is, when the dissociation of the gas is zero or negligible,

$$L - RT = RT^2 \frac{d \log C}{dT}. \qquad (19)$$

When $i = 2$, that is, when the dissociation of the gas is complete,

$$L - 2RT = 2RT^2 \frac{d \log C}{dT}. \qquad (20)$$

Equations (19) and (20) are evidently in harmony with results previously obtained.

Applying the above considerations to the case in which a solid dissolves in a liquid and suffers dissociation, the heat of solution, H_s, of one mole of the solid will correspond to $-(L - iRT)$ since virtually no external work is done, and H_{ds}, the heat evolved when one mole of the dissolved substance dissociates, will correspond to H_v. The concentration, C, of the dissolved substance, is the analytical concentration based on the normal molecular weight of the solute. We therefore have

$$\left.\begin{aligned} H_s &= -\frac{2}{3 - i} RT^2 \frac{d \log C}{dT} + \frac{(i - 1)(2 - i)}{(3 - i)} H_{ds} \\ &= -\frac{2}{2 - \alpha} RT^2 \frac{d \log C}{dT} + \frac{\alpha(1 - \alpha)}{(2 - \alpha)} H_{ds}. \end{aligned}\right\} \qquad (21)$$

H_s is of course strictly the heat of solution of one mole of the solid in a large amount of the saturated solution of concentration C. When the dissociation is negligible ($i = 1$) and when it is

nearly complete ($i = 2$), equation (21) assumes the simple forms corresponding to equations (19) and (20).

It is to be carefully noted that in the cases just considered (liquid N_2O_4 in equilibrium with the gas phase, or a solid in contact with the saturated solution) p, C, α, i, etc., are determined by the temperature alone. In particular in equation (17) where

$$-\frac{H_v}{RT^2} = \frac{d \log K_c}{dT} = \frac{d \log C}{dT} + \frac{3 - i}{(i - 1)(2 - i)} \cdot \frac{di}{dT},$$

both C and i are determined by T alone. If, however, we have the gas (N_2O_4, NO_2) by itself or a solution by itself, the degree of dissociation α (and therefore i) is a function of both T and C (or V). In this case $\frac{di}{dT}$ becomes indefinite unless we specify how C is to vary. Thus we may keep C constant by maintaining the volume unchanged and that is what naturally occurs in the case of liquid solutions, the volume of which does not alter appreciably with change in temperature. Thus in a solution of acetic acid of molar concentration C, the heat of dissociation H_{ds} will be given by the expression (compare equation (17))

$$H_{ds} = -\frac{3 - i}{(i - 1)(2 - i)} RT^2 \left(\frac{di}{dT}\right)_C = -\left(\frac{2 - \alpha}{1 - \alpha}\right) RT^2 \left(\frac{d \log \alpha}{dT}\right)_C, \tag{22}$$

where $\left(\frac{di}{dT}\right)_C$ and $\left(\frac{d \log \alpha}{dT}\right)_C$ are the partial derivatives at constant concentration.

It is also to be noted that in equation (21) the second term is usually small, being zero for $\alpha = 0$ and $\alpha = 1$, and in the case of electrolytic dissociation, H_{ds} is comparatively small. The maximum value of $\frac{(i - 1)(2 - i)}{(3 - i)}$ or of $\frac{\alpha(1 - \alpha)}{(2 - \alpha)}$ is 0.172, when $\alpha = 0.586$, so that the effect of the term $\frac{\alpha(1 - \alpha)}{(2 - \alpha)}$ is usually negligible. It may also be remarked that equation (21) assumes the following simple forms, (a) when α is small, (b) when α approaches unity:

$$H_s = -\left(1 + \frac{\alpha}{2}\right) RT^2 \frac{d \log C}{dT} \text{ (α small).} \qquad (21a)$$

$$H_s = -2\,\alpha RT^2 \frac{d \log C}{dT} \text{ (α approx. = 1).} \qquad (21b)$$

We can find the conditions under which H_s is equal to $-iRT^2 \frac{d \log C}{dT}$ where C is the concentration of a saturated solution. Evidently from equation (14),

$$H_s = -iRT^2 \frac{d \log (iC)}{dT},$$

and if i is constant in saturated solutions,

$$H_s = -iRT^2 \frac{d \log C}{dT}. \qquad (23)$$

If i is constant, then from (17),

$$\frac{d \log C}{dT} = \frac{d \log K_c}{dT}$$

and hence

$$H_s = iH_{ds}.$$

If then the heat evolved, when one mole of a solid dissolves in the saturated solution, is equal to i times the heat of ionization or dissociation, the value of i is constant in all saturated solutions and therefore the degree of dissociation is constant in all saturated solutions. Under these circumstances equation (23) holds. It should be borne in mind, however, that the condition, $H_s = iH_{ds}$, will be fulfilled in but very few cases.

Determining the Degree of Ionization

Methods of determining the degree of dissociation of electrolytes in solution may be divided into two or three classes: in the first class are those which depend on the application of van't Hoff's laws of osmotic pressure, i.e., on the application of the ideal gas laws to the dissolved substances; here we have methods based on the measurement of the osmotic pressure, freezing-point, boiling-point or vapor pressure of solutions. In the second class, we have the method based on the determination of

the conductance of solutions, the degree of dissociation being given, at least approximately, by the ratio of the molecular conductance of the given solution to the molecular conductance at infinite dilution. In a third division may be placed methods depending on measurements of the electromotive force of cells. The accuracy of the methods of the first type depends on whether the behavior of the dissolved substances is represented accurately by the gas laws. In the second type of method, allowances must be made for the change in viscosity of the solution and for the change in mobilities of the ions with changing concentrations. And in all methods the correct interpretation of the results is conditioned by correct assumptions as to the nature of the substances present in the solution. Association of the solute and the presence of complex or intermediate ions frequently render the experimental results exceedingly difficult to interpret.

Ionic Product or Solubility Product

In the case of equilibrium between a very slightly soluble salt and a saturated aqueous solution, the dissolved salt will be almost entirely in the form of its ions. We may consider as an example the solubility of AgCl in water. We shall represent the equilibrium as follows:

$$\underset{\text{solid}}{AgCl} \rightleftarrows \underset{\text{undiss.}}{AgCl} \rightleftarrows \overset{+}{Ag} + \overset{-}{Cl}. \qquad (24)$$

So long as solid AgCl is present, the concentration of undissociated AgCl will be constant at a given temperature and hence in the expression for the equilibrium between the undissociated salt and its ions, the concentration of undissociated salt is a constant. Hence, we may write

$$K_c = [\overset{+}{Ag}] \times [\overset{-}{Cl}] = \text{ionic or solubility product.} \qquad (25)$$

If water is saturated with pure silver chloride and if C is the analytical concentration of dissolved silver chloride in moles per liter, then, since the dissolved salt is almost completely ionized, $C = [\overset{+}{Ag}] = [\overset{-}{Cl}] = \sqrt{K_c}$ or in this case the solubility is equal to the square root of the solubility product. If in a solution we

have silver chloride together with some other chloride such as KCl, we shall still have $K_c = [\overset{+}{Ag}] \times [\overset{-}{Cl}]$. In this case the analytical solubility of silver chloride will be equal to the concentration of $\overset{+}{Ag}$. Hence if K_c, the solubility product, is known, and if the chloride-ion concentration is known, the solubility of the silver chloride can be calculated. Similarly the solubility product for the salt $BaSO_4$ will be $[\overset{++}{Ba}] \times [\overset{=}{SO_4}]$ and for the salt PbI_2 will be $[\overset{++}{Pb}] \times [\overset{-}{I}]^2$. Thus assuming PbI_2 to be completely ionized in aqueous solution and representing by C the analytical concentration of the salt, we shall have $[\overset{++}{Pb}] = C$ and $[\overset{-}{I}] = 2C$ and hence $K_c = [\overset{++}{Pb}] \times [\overset{-}{I}]^2 = 4C^3$.

It may be remarked at this point that experiment has shown that the law of the constancy of the solubility product holds with a fair degree of accuracy even in cases where the law of mass action as applied to the equilibrium between the ions and the undissociated substance does not hold.

Heat of Ionization of Water

According to the theory of free ions, the heat evolved when dilute solutions of an active base and an active acid are mixed is due simply to the union of hydrogen and hydroxyl ions to form water. The heat of neutralization per gram equivalent of strong acid and strong base according to Wörmann * is given by the expression

$$H_n = 14{,}617 - 48.5\,t, \tag{26}$$

where t is the centigrade temperature. If H_{ds} is the heat of dissociation of water represented by the equation

$$H_2O \rightleftarrows \overset{+}{H} + \overset{-}{OH}, \tag{27}$$

then H_{ds} should equal $-14{,}617 + 48.5\,t$. From measurements on the conductance of pure water, Kohlrausch and Heydweiller conclude that the concentration of hydrogen-ion (or hydroxyl-ion) at 18° C. is 0.80×10^{-7} and at 34° C. is 1.47×10^{-7}. The

* Ann. d. Physik., [4] **18**, 793 (1905).

equilibrium constant for the reaction (27) is represented by K_w and is equal to $[\overset{+}{H}] \times [\overset{-}{OH}]$. The heat evolved in the dissociation of one mole of water, H_{ds}, is therefore

$$H_{ds} = -\frac{RT_1T_2}{T_2 - T_1} \log \frac{1.47}{0.80} = -13{,}500 \text{ calories.}$$

This will hold for an average temperature of 26° C., a result in excellent agreement with that calculated from equation (26) viz., −13,356 calories.

Heat of Ionization of Various Electrolytes

If we assume that the degree of ionization α of a solution of a binary electrolyte is given accurately by the relation $\alpha = \frac{\lambda}{\lambda_\infty}$, where λ is the equivalent conductance of the solution and λ_∞ the equivalent conductance at infinite dilution, then equation (22) may be written

$$H_{ds} = -\frac{2-\alpha}{1-\alpha} RT^2 \left(\frac{d \log \alpha}{dT}\right)_C = \frac{2\lambda_\infty - \lambda}{\lambda_\infty - \lambda}\left[\frac{1}{\lambda_\infty}\frac{d\lambda_\infty}{dT} - \frac{1}{\lambda}\frac{d\lambda}{dT}\right]. \quad (28)$$

The heat of dissociation of binary electrolytes can therefore be calculated from measurements of the equivalent conductance at different temperatures, the values of λ_∞ at the different temperatures being assumed to be known.

Other methods of determining the heats of ionization may be applied in certain cases. Thus the heat of dissociation of a weak base BOH can be calculated from the heat of neutralization using a strong acid such as HCl. If the neutralization is carried out in dilute solution so that the strong acid is almost completely dissociated, the thermochemical equation for the reaction, according to the theory of free ions, is

$$BOH + \overset{+}{H} \rightarrow \overset{+}{B} + H_2O + H_n \text{ calories.} \quad (29)$$

This reaction may be supposed to take place in the following two stages:

$$BOH \rightarrow \overset{+}{B} + \overset{-}{OH} + H_{ds}.$$

$$\overset{-}{OH} + \overset{+}{H} \rightarrow H_2O + 13{,}700 \text{ calories.}$$

Accordingly, taking $-13{,}700$ calories as the heat of dissociation of water, we have, for the dissociation of the weak base.

$$H_{ds} = H_n - 13{,}700. \tag{30}$$

Evidently equation (30) assumes that the weak base is entirely undissociated and that the acid and salt are completely dissociated. It is therefore only an approximation formula. A similar method could be used in the case of a weak acid, using a strong base, such as NaOH, for neutralization.

The heats of ionization of weak bases or weak acids may also be determined by the following method. To a solution of a salt of the weak base or weak acid add an equivalent amount of a strong base or strong acid respectively. The heat effect will be the negative heat of ionization of the weak electrolyte. Thus if to a solution of KCN we add HCl or to a solution of NH_4Cl we add NaOH, we shall have the following reactions according to the theory of ionization:

$$\left.\begin{aligned} \overset{+}{K} + \overset{-}{CN} + \overset{+}{H} &\rightarrow \overset{+}{K} + HCN - H_{ds}, \\ \overset{+}{NH_4} + \overset{+}{Na} + \overset{-}{OH} &\rightarrow \overset{+}{Na} + NH_4OH - H_{ds}. \end{aligned}\right\} \tag{31}$$

In these cases, also, account must be taken of the fact that the strong electrolytes are not completely dissociated and the weak acids or bases are not entirely undissociated.

Effect of Common Ion

If acetic acid and sodium acetate are brought together in aqueous solution, we shall of course have $HC_2H_3O_2$, $\overset{+}{H}$ and $\overset{-}{C_2H_3O_2}$ in equilibrium and also $NaC_2H_3O_2$, $\overset{+}{Na}$ and $\overset{-}{C_2H_3O_2}$ in equilibrium. The characteristic feature of this case is that one substance, viz.: $\overset{-}{C_2H_3O_2}$, takes part in two different reactions. Thus we shall have the equations

$$\left.\begin{aligned} HC_2H_3O_2 &\rightleftarrows \overset{+}{H} + \overset{-}{C_2H_3O_2}, \\ NaC_2H_3O_2 &\rightleftarrows \overset{+}{Na} + \overset{-}{C_2H_3O_2}. \end{aligned}\right\} \tag{32}$$

We have selected for purposes of illustration a weak acid and

therefore slightly ionized and a salt of the acid, the salt being highly dissociated. The equilibrium between $NaC_2H_3O_2$, $\overset{+}{Na}$ and $\overset{-}{C_2H_3O_2}$ will hardly be affected by the addition of acetic acid, since the latter will furnish a negligible concentration of $\overset{-}{C_2H_3O_2}$ in comparison with that due to the dissociation of the salt. The presence of the salt will however affect the dissociation of the acid to a remarkable extent. Thus in a normal solution of acetic acid at 25° C. (see Table XXII) assuming $K = 0.0000180$, we shall have $[HC_2H_3O_2] = 0.99587$ and $[\overset{+}{H}] = [\overset{-}{C_2H_3O_2}] = 0.00423$. If to this solution we add solid $NaC_2H_3O_2$, we can easily obtain a concentration of $\overset{-}{C_2H_3O_2}$ equal to unity, due to the dissociation of the salt. Let us calculate the equilibrium concentration of $HC_2H_3O_2$ and $\overset{+}{H}$. Equilibrium will be reached when $\overset{+}{H}$ and $\overset{-}{C_2H_3O_2}$ by uniting to form $HC_2H_3O_2$ have reached values satisfying the equilibrium conditions. If x represents the decrease in the concentration of $\overset{+}{H}$, we shall have

$$K = 0.0000180 = \frac{(0.00423 - x)\ (1.00423 - x)}{(0.99577 + x)}. \qquad (33)$$

Since x must be less than 0.00423, we can as a first approximation write

$$0.0000180 = \frac{(0.00423 - x)\ 1.00423}{0.9958}, \qquad (34)$$

whence $(0.00423 - x) = 0.0000179 = [\overset{+}{H}]$ at equilibrium. Hence $x = 0.004212$. Using this value of x in equation (33), we obtain the following values at equilibrium, $[HC_2H_3O_2] = 0.99998$, $[\overset{+}{H}] = 0.0000180$, and $[\overset{-}{C_2H_3O_2}] = 1.000$. The addition of the salt with a common ion has reduced the concentration of $\overset{+}{H}$ to a value 235 times as small as the original value.

Hydrolysis

Hydrolysis is a process in which a salt and water react to form free acid and free base; it is therefore the exact reverse of neu-

tralization. Since neutralization is in general a fairly complete process, hydrolysis will usually be almost negligible. We shall deduce expressions for the hydrolysis of salts (1) of a strong acid and weak base, (2) of a strong base and weak acid, and (3) of a weak acid and weak base.

(1) Salt of weak base and strong acid.

We may take as an example of this class, the chloride, MCl, of a weak base MOH. The equation representing the hydrolysis may be written

$$MCl + H_2O \rightleftarrows MOH + HCl, \tag{35}$$

and the hydrolytic equilibrium constant K_h will be, since the concentration of the water may be assumed to be constant,

$$K_h = \frac{[MOH] \times [HCl]}{[MCl]}. \tag{36}$$

From the ionic point of view, assuming the weak base, MOH, to be almost completely undissociated and the acid, HCl, and the salt, MCl, to be ionized to the same extent, we have

$$K_h = \frac{[MOH] \times [\overset{+}{H}]}{[\overset{+}{M}]}, \tag{37}$$

corresponding to the ionic equation (38) which takes the place of (35),

$$\overset{+}{M} + H_2O \rightleftarrows MOH + \overset{+}{H}. \tag{38}$$

Multiplying the numerator and denominator of (37) by $[\overset{-}{OH}]$ we obtain

$$K_h = \frac{[MOH]}{[\overset{+}{M}] \times [\overset{-}{OH}]} \cdot [\overset{+}{H}] \times [\overset{-}{OH}] = \frac{K_w}{K_B}, \tag{39}$$

where K_B and K_w are the dissociation constants of the weak base and of water respectively. Let C be the analytical concentration of the salt in moles per liter and $V = \frac{1}{C}$ be the dilution. Let h be the fraction hydrolyzed, and let α be the degree of dissociation. Then $[\overset{+}{M}] = C\,(1 - h)\,\alpha$, and $[MOH] = C\,h$. Also $[\overset{+}{H}] = C\,h\,\alpha$

if we assume the acid and salt to have equal degrees of ionization. Substituting in equation (37) we obtain

$$K_h = \frac{Ch^2}{1-h} = \frac{h^2}{(1-h)\,V} = \frac{K_w}{K_B}. \tag{40}$$

(2) Salt of strong base and weak acid.

Let NaA represent the salt of the strong base, NaOH, and the weak acid, HA. The equations representing the hydrolysis will be

$$\left.\begin{aligned} &NaA + H_2O \rightleftarrows NaOH + HA \\ &\overset{-}{A} + H_2O \rightleftarrows \overset{-}{OH} + HA \text{ (ionic equation)} \end{aligned}\right\}. \tag{41}$$

Assuming the salt NaA and the base NaOH to be equally dissociated in the solution, we arrive at results analogous to those in the previous section by substituting K_A, the dissociation constant of the weak acid, for K_B. Thus we obtain

$$K_h = \frac{Ch^2}{1-h} = \frac{h^2}{(1-h)\,V} = \frac{K_w}{K_A}. \tag{42}$$

(3) Salt of weak base and weak acid.

Let MA represent the salt of the weak base, MOH, and the weak acid, HA. Then $[\overset{+}{M}] = [\overset{-}{A}] = C(1-h)\alpha$. We have as the equation for the hydrolysis

$$\left.\begin{aligned} &MA + H_2O \rightleftarrows MOH + HA \\ &\overset{+}{M} + \overset{-}{A} + H_2O \rightleftarrows MOH + HA \text{ (ionic form)} \end{aligned}\right\}. \tag{43}$$

Now, $[MOH] = [HA] = Ch$ and

$$K_h = \frac{[MOH] \times [HA]}{[\overset{+}{M}] \times [\overset{-}{A}]} = \frac{[MOH]}{[\overset{+}{M}] \times [\overset{-}{OH}]} \times \frac{[HA]}{[\overset{+}{H}] \times [\overset{-}{A}]}$$

$$\times [\overset{+}{H}] \times [\overset{-}{OH}] = \frac{K_w}{K_A K_B} = \frac{C^2h^2}{C^2(1-h)^2\alpha^2}$$

$$= \frac{h^2}{\alpha^2(1-h)^2} = \frac{h^2}{(1-h)^2} \text{ approx.} \tag{44}$$

Since α, the degree of dissociation of the salt, does not vary much with change in concentration, we can infer that the degree of hydrolysis of a salt of a weak acid and weak base (for example aniline acetate) will be independent of the dilution. This has

been confirmed experimentally. Thus in the case of aniline acetate, Lundén * found that for dilutions of 39.32 and 195.9 liters per mole, the degree of hydrolysis at 25° C. was 51.3 and 52.3 per cent respectively.

A more rigorous analysis of the problem of the hydrolysis of the salt of a weak base and a weak acid leads to the following expression:

$$K_h = \frac{K_w}{K_A K_B} = \frac{h^2}{\alpha_s^2 (1-h)^2} \cdot \frac{(1-\alpha_A)(1-\alpha_B)}{\left(1+\frac{h\alpha_A}{(1-h)\alpha_s}\right)\left(1+\frac{h\alpha_B}{(1-h)\alpha_s}\right)}, \tag{45}$$

where α_A, α_B and α_s are the degrees of dissociation of the acid, base and salt respectively. In general α_s is approximately unity and α_A and α_B are extremely small, so that equation (45) is essentially the same as the result given in equations (44).

In general, hydrolysis is evident by the fact that the aqueous solution of the salt reacts either acid or alkaline to indicators. It will be evident however that if the weak base and weak acid are of equal strengths, so that $K_A = K_B$, then, although there will be hydrolysis, the concentration of $\overset{+}{H}$ will equal that of $\overset{-}{OH}$ and the solution will be neutral.

Two Weak Electrolytes with Common Ion

Since virtually all salts are strong electrolytes, we are concerned here with solutions containing two weak acids or two weak bases. We must also bear in mind that water may be considered as both a weak base and a weak acid. Thus in an aqueous solution of the weak acid HA, we shall have

$$K_A = \frac{[\overset{+}{H}] \times [\overset{-}{A}]}{[HA]}; \qquad K_w = [\overset{+}{H}] \times [\overset{-}{OH}];$$
$$[\overset{+}{H}] = [\overset{-}{A}] + [\overset{-}{OH}]. \tag{46}$$

Since $[\overset{-}{OH}] = [\overset{+}{H}] - [\overset{-}{A}]$, $\qquad K_w = [\overset{+}{H}]^2 - [\overset{+}{H}] \times [\overset{-}{A}]$,

and hence
$$[\overset{+}{H}]^2 = K_w + K_A [HA], \tag{47}$$

* Jour. chim. phys., **5**, 155 (1906).

which is the strict formula for the dissociation of a weak acid in water. In general, K_w is negligible in comparison with K_A [HA], and $[\overset{-}{OH}]$ is negligible in comparison with $[\overset{+}{H}]$, so that (47) becomes the ordinary Ostwald dilution formula, $[\overset{+}{H}] \times [\overset{-}{A}] = K_A$ [HA]. Similarly for a weak base, MOH, in water, we should have

$$[\overset{-}{OH}]^2 = K_w + K_B\,[MOH]. \tag{48}$$

Let us now consider an aqueous solution of two weak acids HA_1 and HA_2, whose dissociation constants are K_1 and K_2 respectively. Analogously to equation (47) we shall have

$$[\overset{+}{H}]^2 = K_w + K_1\,[HA_1] + K_2\,[HA_2]. \tag{49}$$

In general, K_w can be neglected in this equation. Let α_1 and α_2 be the degrees of dissociation, and C_1 and C_2 the concentrations of the two acids. Then

$$K_1 = \frac{\alpha_1\,(C_1\alpha_1 + C_2\alpha_2)}{1 - \alpha_1}; \quad K_2 = \frac{\alpha_2\,(C_1\alpha_1 + C_2\alpha_2)}{1 - \alpha_2}. \tag{50}$$

Let us consider the case in which the two acids are of equal strength, i.e. $K_1 = K_2$. Then from (50), it follows that $\alpha_1 = \alpha_2$. In other words, in a solution of two acids which have the same dissociation constant, both acids are dissociated to the same extent, no matter what their concentrations may be. Let us call this degree of dissociation, α. Then under these circumstances, we have

$$K_1 = K_2 = \frac{(C_1 + C_2)\alpha^2}{1 - \alpha}. \tag{51}$$

Comparing (51) with equation (7), we express our result in the following way: In a solution of two acids possessing equal dissociation constants, each acid has the same degree of dissociation which it would have if it were present alone at a concentration equal to the sum of the concentrations $(C_1 + C_2)$ of the acids. This same rule is often used in the case of a solution of two strong acids or two salts with a common ion since strong acids and salts may be supposed to have approximately equal dissociation constants.

Moreover, if we have two solutions of acids of equal dissociation constants, there will in general be a change in the degree of dissociation on adding one to the other. If however their original concentrations are equal, the total concentration after mixing in any proportion will be the same as that of each before mixing and there will be no change in the degree of dissociation.

Let us however consider the case in which solutions of acids of different concentrations are mixed. Let V_1 liters of the solution of acid of concentration C_1 and equilibrium constant K_1 be added to V_2 liters of the acid of concentration C_2 and dissociation constant K_2. Let α_1 and α_2 be the degrees of dissociation of the acids in the mixture. Then we shall obtain

$$K_1 = \frac{\alpha_1}{1 - \alpha_1}\left(\frac{V_1}{V_1 + V_2} C_1\alpha_1 + \frac{V_2}{V_1 + V_2} C_2\alpha_2\right);$$
$$K_2 = \frac{\alpha_2}{1 - \alpha_2}\left(\frac{V_1}{V_1 + V_2} C_1\alpha_1 + \frac{V_2}{V_1 + V_2} C_2\alpha_2\right). \qquad (52)$$

Let us take the case in which $C_1\alpha_1 = C_2\alpha_2$. Then we shall have

$$K_1 = \frac{C_1\alpha_1^2}{1 - \alpha_1}; \quad K_2 = \frac{C_2\alpha_2^2}{1 - \alpha_2}. \qquad (53)$$

Evidently α_1 and α_2 are the same as the degrees of dissociation before mixing and the equation $C_1\alpha_1 = C_2\alpha_2$ means that both solutions had the same hydrogen-ion concentration before mixing. Hence we can say that if two weak acids have the same hydrogen-ion concentration they may be mixed in any proportion without changing the degree of dissociation of either acid. In addition the hydrogen-ion concentration of the mixture will be the same as that of either acid before mixing.

The results obtained in the case of two weak acids may be easily transferred to the case in which two weak bases are considered.

Amphoteric Electrolytes

A class of substances is known which possess both basic and acidic properties and on ionization can furnish both hydrogen and hydroxyl ions. The amino-acids may be taken as typical examples. In the hydrated form, they may be represented by the

general formula, HXOH. Thus glycollic acid, NH_2CH_2COOH, may be considered to exist in the hydrated form $OH \cdot NH_3CH_2COOH$. The theory of the behavior of such substances, called in general amphoteric electrolytes, was first given by Walker.*

In the first place, it will be clear that for any equilibrium $R + nH_2O \rightleftarrows R(H_2O)_n$, the ratio of the anhydrous to the hydrated form is a constant independent of the dilution, provided the solution may be considered a dilute one. If then any function is proportional to [R], it will also be proportional to $[R(H_2O)_n]$ and also to the sum of [R] and $[R(H_2O)_n]$.

In an aqueous solution of the amphoteric electrolyte, we shall have the following sets of equilibria to consider:

$$HXOH \rightleftarrows \overset{+}{H} + \overset{-}{OH} + X \rightleftarrows H_2O + X \tag{54a}$$

$$HXOH \rightleftarrows \overset{+}{H} + \overset{-}{X}OH \tag{54b}$$

$$HXOH \rightleftarrows \overset{-}{O}H + \overset{+}{X}H \tag{54c}$$

$$H_2O \rightleftarrows \overset{+}{H} + \overset{-}{OH} \tag{54d}$$

Let our solution contain C moles of the amphoteric electrolyte per liter and let us represent the concentrations of the various substances present in the following manner: $[\overset{+}{H}] = a$; $[\overset{-}{OH}] = b$; $[\overset{-}{X}OH] = d$; $[\overset{+}{X}H] = e$; $[X] + [HXOH] = u$. Let K_w be the dissociation constant of water, K_A and K_B the dissociation constants of the amphoteric electrolyte as acid and as base respectively. Then from equations (54a)–(54d), we shall have

$$ab = K_w. \tag{58a}$$

$$ad = K_A u \ (u \text{ is proportional to } [HXOH]). \tag{58b}$$

$$be = K_B u. \tag{58c}$$

$$a + e = b + d \text{ (electroneutrality of solution).} \tag{58d}$$

$$u + d + e = C. \tag{58e}$$

The five equations (58a)–(58e) determine any five of the quantities (for example, a, b, d, e and u) in terms of the remaining four quantities (for example, K_w, K_A, K_B, C).

* Proc. Roy. Soc., **73** and **74** (1904). Z. f. physik. Chem., **49,** 82 (1904); **51,** 706 (1905).

The general solution of these equations will lead to very complicated expressions. We shall content ourselves with a few particular solutions. In the first place, we shall assume that $K_A = K_B$; i.e., that the amphoteric electrolyte is equally strong as a base and as an acid. From (58b) and (58c), it follows that $ad = be$ or $\frac{a}{e} = \frac{b}{d}$; hence $\frac{a+e}{e} = \frac{b+d}{d}$ and therefore from (58d), $d = e$. Hence $a = b$. Since $ab = K_w = a^2 = b^2$, it follows that in this case the solution is neutral for all dilutions, $[\overset{+}{H}] = [\overset{-}{OH}] = \sqrt{K_w} = 10^{-7}$ at 25° C. We have therefore when $K_A = K_B$, $a = b = \sqrt{K_w}$; $ad = K_A u$; $u + 2d = C$. Eliminating a and d, we obtain

$$\frac{u}{C} = \frac{1}{1 + \frac{2K_A}{\sqrt{K_w}}} = \text{(fraction undissociated)}. \qquad (59)$$

The fraction dissociated is $\frac{2d}{C} = 1 - \frac{u}{C}$ or

$$1 - \frac{u}{C} = \frac{2K_A}{2K_A + \sqrt{K_w}}. \qquad (60)$$

We therefore obtain the result that in the case of an amphoteric electrolyte for which $K_A = K_B$, the degree of dissociation is independent of the dilution. If we take as an example a substance for which $K_A = K_B = 10^{-7}$, the degree of dissociation at all dilutions would be 66.7 per cent, a rather surprising result.

We may next consider the case of *o*-aminobenzoic acid for which $K_A = 1.04 \times 10^{-5}$ and $K_B = 1.34 \times 10^{-12}$. For a solution which is $\frac{N}{64}$, we obtain the following values:

$$C = 0.015625; \quad u = [X] + [HXOH] = 0.01451;$$
$$a = [\overset{+}{H}] = 2.264 \times 10^{-4}; \quad b = [\overset{-}{OH}] = 4.417 \times 10^{-11};$$
$$d = [\overset{-}{XOH}] = 6.667 \times 10^{-4}; \quad e = [\overset{+}{HX}] = 4.403 \times 10^{-4}.$$

At a dilution of 64 liters, the acid is 92.93 per cent undissociated and 7.07 ionized. At this dilution if K_B were zero, $[\overset{+}{H}]$ would equal $[XOH] = 3.984 \times 10^{-4}$, corresponding to 2.55 per cent

ionization. It will be seen that the concentration of $\overset{+}{HX}$ due to the ionization as a base is almost double that of $\overset{+}{H}$ although less than that of the negative ion $\overset{-}{X}OH$. It will be clear that if the degree of dissociation of this amphoteric electrolyte were calculated in the ordinary way from conductance measurements making the usual assumptions, erroneous values would be obtained and the law of mass action would seem to be invalid.

Strong Electrolytes

We may conclude this chapter with a consideration of the equilibrium in a solution of a strong electrolyte, viz.: an active acid, active base or a salt. As has been repeatedly pointed out, Ostwald's dilution formula does not hold for such solutions, so that we may not write for a solution of NaCl, $K = \frac{[\overset{+}{Na}] \times [\overset{-}{Cl}]}{[NaCl]}$.

A large number of expressions have been put forward of which the following may be taken as representative:

(a) Rudolphi * (1895) $\frac{C^{\frac{1}{2}}\alpha^{\frac{1}{2}}}{1-\alpha} = K.$

(b) Van't Hoff † (1895) $\frac{C^{\frac{1}{2}}\alpha^{\frac{1}{2}}}{1-\alpha} = \frac{(C\alpha)^{\frac{1}{2}}}{C(1-\alpha)} = K.$

(c) Partington ‡ (1910) $\frac{C\alpha^2}{1-\alpha} = K + K'C\alpha.$

(d) MacDougall § (1912) $\frac{C\alpha^2}{1-\alpha} = K[1 + m(C\alpha)^n].$

(e) Kendall ¶ (1912) $\frac{C\alpha^2}{1-\alpha} = K + K'\left(\frac{1-\alpha}{\alpha}\right).$

(f) Kraus & Bray || (1913) identical with (d).

(g) Bates ** (1915), $\log\left(\frac{C\alpha^2}{1-\alpha}\right) = K + K'(C\alpha)^h.$

* Z. f. physik. Chem., **17,** 385 (1895).
† Z. f. physik. Chem., **18,** 301 (1895).
‡ Trans. Chem. Soc., **97,** 1158, (1910).
§ Jour. Amer. Chem. Soc., **34,** 855 (1912).
¶ Trans. Chem. Soc., **101,** 1283 (1912).
|| Jour. Amer. Chem. Soc., **35,** 1412 (1913).
** Jour. Amer. Chem. Soc., **37,** 1431 (1915).

The formulas of Rudolphi and van't Hoff are purely empirical attempts to represent the relation between C and α over certain ranges of concentration. The others attempt to give expression to the fact that the activity (see equation (9) and the statement immediately following it) of the undissociated substance is greater than its concentration when ions are present. This may be expressed in terms of the kinetic view of ionic equilibrium by saying that the rate at which a substance dissociates is proportional to its concentration only in the absence of ions; when the ionic concentration is appreciable, the rate of dissociation increases more rapidly than the concentration. Thus formula (d) may be written $K = \frac{C\alpha \times C\alpha}{C(1-\alpha)\,[1 + m(C\alpha)^n]}$ for the dissociation of a salt into two ions. In this equation the activity of the ions would be equal to their concentration, $C\alpha$; but the activity of the undissociated substance would be $[1 + m(C\alpha)^n]$ times the concentration $C(1-\alpha)$. For further details, the original articles should be consulted.

PROBLEMS

1. A weak monobasic acid is ionized to the extent of one per cent in tenth-normal solution. What is the value of the dissociation constant? What will be the degree of dissociation in hundredth-normal solution?

2. The solubility of AgCl in water at 9.97° is 8.9×10^{-5} per cent and at 25.86° is 1.94×10^{-4} per cent. Calculate the heat of solution of a mole of AgCl.

3. A saturated aqueous solution of TlCl contains at 25° C. and at 39.7° C., 0.386 and 0.604 per cent respectively of the salt. Calculate the heat of solution of 1 mole of TlCl assuming an average degree of dissociation of 90 per cent.

4. A saturated aqueous solution of $BaSO_4$ at 25° C. contains 2.3×10^{-4} per cent of the salt. Calculate the solubility product. What will be the solubility of $BaSO_4$ in 0.2 N $(NH_4)_2SO_4$, assuming the latter to be completely dissociated.

5. A saturated aqueous solution of PbI_2 contains at 25° C., 0.00165 mole of the salt per liter. Determine the ionic product. What will be the solubility of PbI_2 in a solution containing 10 grams of NaI per 100 cc. Assume NaI to be completely ionized.

6. The following heats of formation at constant pressure are due to Thomsen: (H, Cl, Aq) = 39,320, (K, C, N, Aq) = 29,490, [H, C, N, Aq]

$= -21{,}380$, and (K, Cl, Aq) = 101,170 calories. From these data calculate the heat of ionization of hydrocyanic acid, assuming the three other substances to be completely dissociated in solution.

7. The heat of neutralization of HCN by a dilute solution of NaOH is 2770 calories. Calculate the heat of ionization of HCN.

8. Given the following heats of formation: (N, H_4, Cl, Aq) = 71,910; (Na, O, H, Aq) = 111,810; (Na, Cl, Aq) = 96,510 and (N, H_4, O, H, Aq) = 88,680; calculate the heat of ionization of NH_4OH.

9. The heat of neutralization of NH_4OH by HClAq is 12,270 calories; calculate the heat of ionization of NH_4OH.

10. Calculate the concentration of $\overset{+}{H}$ in $\frac{N}{100}$ acetic acid, if K_A = 0.00001 80. If 0.01 mole of solid $NaC_2H_3O_2$ is added to a liter of the acid solution, calculate the final hydrogen-ion concentration, assuming the salt to be completely dissociated.

11. Taking K_B for NH_4OH equal to 1.8×10^{-5} and $K_w = 1 \times 10^{-14}$ at 25° C., calculate the degree of hydrolysis at 25° C. of aqueous solutions of NH_4Cl containing 1 mole of the salt (a) in 36 liters (b) in 100 liters.

12. What is the degree of hydrolysis at 25° C. of the following solutions: N, $\frac{N}{10}$ and $\frac{N}{100}$ KCN, given $K_w = 10^{-14}$ and K_A for HCN $= 7.2 \times 10^{-10}$?

13. A solution of potassium phenolate, C_6H_5OK, containing 1 mole in 51.3 liters is hydrolyzed 6.69 per cent at 25° C. Assuming $K_w = 10^{-14}$, calculate the dissociation constant of phenol as an acid.

14. At 25° C., a tenth-molar solution of aniline hydrochloride is hydrolyzed 1.56 per cent. Calculate the hydrolytic constant and the dissociation constant of aniline as a base.

15. What would be the percentage hydrolysis in $\frac{N}{10}$ aniline hydrochloride if the solution were also $\frac{N}{100}$ with respect to HCl (assumed completely dissociated)?

16. Calculate the percentage hydrolysis at 25° C. in $\frac{N}{10}$ $NH_4C_2H_3O_2$ if $K_A = K_B = 1.8 \times 10^{-5}$ and $\alpha = 0.82$.

17. Calculate the percentage hydrolysis at 25° C. of $\frac{N}{100}$ aniline acetate assuming the salt to be (a) 100 per cent dissociated; (b) 90 per cent dissociated. Obtain K_A and K_B from problems 10 and 14.

18. Calculate the degree of dissociation of an aqueous solution of acetoxime, CH_3CHNOH, if $K_A = K_B = 6.3 \times 10^{-13}$ at 25° C.

CHAPTER XVII

ELECTROMOTIVE FORCE

According to equation (9), Chap. IX, the total amount of work obtainable in a reversible isothermal process is equal to the decrease in the free energy of the system. For our present purpose, we may say that the total work may appear in two forms, viz.: electrical energy and mechanical work due to changes in volume. If we restrict our consideration to processes either at constant volume or at constant pressure, then the purely mechanical work will either be zero (constant volume) or equal to $p\,(V_2 - V_1)$ where p is the constant pressure and V_1 and V_2 are the initial and final volumes. For any reversible isothermal process at constant pressure, we shall have

$$F_1 - F_2 = W = \text{electrical energy obtained} + p\,(V_2 - V_1). \quad (1)$$

Hence

$$\begin{aligned}\text{Electrical work} &= W - p\,(V_2 - V_1)\\ &= F_1 - F_2 + p\,(V_1 - V_2) = (\Phi_1 - \Phi_2)_{T,p}. \quad (2)\end{aligned}$$

We thus obtain the result that the electrical energy obtained in a reversible isothermal process is equal to the decrease in the value of the thermodynamic potential of the system. In Chap. XV, in our study of chemical equilibrium, we found the following relationship between the affinity of a process, $A_p = (\Phi_1 - \Phi_2)_{T,p}$, and the equilibrium constant, (equation (30), Chap. XV),

$$\left.\begin{aligned}A = (\Phi_1 - \Phi_2)_{T,p} &= RT \log K_p - RT\sum \nu_1 \log p_1\\ &= RT \log K_c - RT\sum \nu_1 \log c_1.\end{aligned}\right\} \quad (3)$$

We also found that equation (3), valid for reactions between ideal gases, is also valid for reactions in dilute solutions if we substitute osmotic pressures for gaseous pressures. Since affinity and equilibrium constant are related to the electrical energy

obtainable in a process, the importance of a study of the electromotive force of cells will be immediately apparent.

The electrical energy produced in a circuit is equal to the product of the E.M.F., and the quantity of electricity which flows through the circuit. We shall frequently employ as a unit of quantity of electricity, the faraday, equal to 96,500 coulombs and represented by the symbol F_v. If then the quantity of electricity, nF_v, flows through a circuit in which the E.M.F. is E, the electrical energy produced is nF_vE and if the process occurs isothermally and reversibly at constant pressure, we shall have

$$nF_vE = W - p(V_2 - V_1) = A = \Phi_1 - \Phi_2. \qquad (4)$$

Reversible and Irreversible Cells

Let us imagine the cell, Zn – $ZnSO_4Aq$ – Pt, so arranged as to have in the circuit an opposing E.M.F., the magnitude of which may be varied at will. We shall suppose that at first the E.M.F. of the cell is exactly counterbalanced by the opposing E.M.F., so that no current is flowing. If we increase the opposing E.M.F. slightly, we shall have metallic zinc deposited on the zinc electrode and oxygen evolved on the platinum and in addition sulphuric acid will be formed near the platinum. If now we diminish the opposing E.M.F. so that it is less than that of the cell, metallic zinc will go into solution and hydrogen will be evolved on the platinum. In addition zinc hydroxide will be formed near the platinum. This second process is not the exact reverse of the first. If however we have a cell of the following kind: zinc amalgam$_{\text{concentrated}}$ – $ZnSO_4Aq$ – zinc amalgam$_{\text{dilute}}$, it will be evident that by altering the opposing E.M.F., we can exactly reverse the process that takes place. Or if we have a cell of the Daniell type, Zn – $ZnSO_4Aq$ – $CuSO_4Aq$ – Cu, the process that takes place under certain conditions can be exactly reversed by altering the opposing E.M.F. in a suitable manner. (We neglect the slight changes due to diffusion between the two solutions.) Any cell in which the process which occurs when the current flows in one direction is exactly reversed when the current flows in the opposite direction will be called a reversible

cell. All other cells will be called irreversible. We shall be concerned mainly with reversible cells.

Conventions

When unit quantity of electricity is transported across the boundary separating two different bodies, a certain amount of electrical work is either expended or gained. We must therefore consider the contact of two dissimilar bodies as the seat of a difference of potential. In order to avoid confusion in the interpretation of statements of E.M.F., or of differences of potential, we must adopt a definite convention. Thus, if we write

$$A, B = x \text{ volts}, \tag{5}$$

we shall mean that there is a difference of potential at the contact of A and B amounting to x volts, and, when x is positive, that there is a tendency for positive electricity to flow across the junction from A to B, that is from left to right. Thus the expression

$$\mathrm{Zn} - \underset{\text{conc.} = c}{\mathrm{ZnSO_4Aq}} = +0.76 \text{ volts} \tag{6}$$

will mean that there is a tendency for the positive current to flow from metallic zinc into the solution. Similarly, when we write

$$\mathrm{Zn} - \underset{c_1}{\mathrm{ZnSO_4}} - \underset{c_2}{\mathrm{CuSO_4}} - \mathrm{Cu} = 1.10 \text{ volts}, \tag{7}$$

we shall mean that this cell has an E.M.F. of 1.10 volts and that the current through the combination is from left to right. If the Zn and Cu are connected by a wire, the current outside the combination will of course be from the copper to the zinc, so that the Cu is the positive pole and the Zn the negative pole. The difference of potential at the junction of two different solutions will be represented in a similar manner. Thus

$$\underset{0.1\,M}{\mathrm{KCl}}, \underset{0.1\,M}{\mathrm{HCl}} = -0.0286 \text{ volt} \tag{8}$$

means that in this case positive electricity tends to pass from right to left.

Instead of equation (7) which represents the arrangement of the substances in the Daniell Cell, we may describe the process

that occurs in the cell by the customary chemical equation and write

$$Zn + \underset{c_2}{CuSO_4} = \underset{c_1}{ZnSO_4} + Cu; \quad E = 1.10 \text{ volts.} \qquad (9)$$

When E is positive, as in equation (9), it means that the cell is capable of furnishing electrical energy when the reaction proceeds from left to right. In all cases great care must be taken to indicate the exact state of all the substances, particularly the partial pressures of the reacting gases and the concentrations of the dissolved substances. The differences of potential at the contact of unlike metals cancel each other in a closed circuit at constant temperature, so that we do not need to consider them. In the combination represented in equation (7) there remain three sources of potential, viz.: the contact $Zn - ZnSO_4$, the contact $CuSO_4 - Cu$ and the liquid junction $ZnSO_4 - CuSO_4$. If it is desired to indicate the E.M.F. of a combination due to the electrode potentials only, we shall make use of the following scheme:

$$Hg, HgCl, \underset{c=1}{KCl} \;\Big\|\; \underset{c=0.1}{HCl}, Cl_2; \quad E = 1.1423,$$

where the two vertical lines indicate that the liquid junction potential is not included in the given value of E.

Let the chemical equation for any process be indicated as follows:

$$\nu_1 A_1 + \ldots = \nu_2 A_2 +$$

and let us suppose that, when this process takes place in a reversible cell at constant temperature and pressure, the quantity of electricity, nF_v, passes through the circuit, then we have according to equations (3) and (4)

$$\left.\begin{aligned} E &= \frac{RT}{nF_v} \log K_p - \frac{RT}{nF_v} \sum \nu_1 \log p_1 \\ &= \frac{RT}{nF_v} \log K_c - \frac{RT}{nF_v} \sum \nu_1 \log c_1. \end{aligned}\right\} \qquad (10)$$

It is customary to deal with the partial pressures of gases and with the concentrations of dissolved substances. If then in any process in which gases and solutions are concerned, we adhere to

this convention, we shall have a new equilibrium constant, K, and in place of equation (10) we shall have

$$E = \frac{RT}{nF_v} \log K - \frac{RT}{nF_v}\left[\sum \nu_1 \log c_1 + \sum \nu_1 \log p_1\right]. \quad (11)$$

It is to be remembered that ν is negative when it refers to a substance on the left side and positive when it refers to a substance on the right side of an equation. The concentrations of solids (or pure liquids) being constant at constant pressure, their values are (as previously explained in Chap. XV, under Reactions in Heterogeneous Systems) included in the equilibrium constant.

Let us apply these considerations to the process occurring in a Daniell Cell. We may describe this process by the equation

$$Zn + \overset{++}{Cu} \rightarrow \overset{++}{Zn} + Cu; \quad \text{E.M.F.} = E \text{ volts}, \quad (12)$$

or we may use the following scheme:

$$Zn - \overset{++}{Zn} \parallel \overset{++}{Cu} - Cu; \quad \text{E.M.F.} = E \text{ volts}. \quad (13)$$

Applying equation (11), we obtain, since $n = 2$,

$$E = \frac{RT}{2F_v} \log K - \frac{RT}{2F_v}\left(-\log [\overset{++}{Cu}] + \log [\overset{++}{Zn}]\right)$$

$$= \frac{RT}{2F_v} \log K - \frac{RT}{2F_v} \log \frac{[\overset{++}{Zn}]}{[\overset{++}{Cu}]}, \quad (13)$$

where $[\overset{++}{Zn}]$ is the concentration of zinc ions and K, the equilibrium constant, is defined by the equation

$$K = \frac{[\overset{++}{Zn}]_e}{[\overset{++}{Cu}]_e}, \quad (14)$$

where the subscript, e, indicates equilibrium concentrations.

As a second illustration, we may take the reaction

$$\left.\begin{aligned} &H_2 \text{ (gas)} + Cl_2 \text{ (gas)} = 2\underset{c = 0.1}{HCl}; \quad \text{E.M.F.} = E \text{ volts} \\ &H_2, \underset{0.1\,M}{HCl}, Cl_2; \quad \text{E.M.F.} = E \text{ volts}. \end{aligned}\right\} \quad (15)$$

Evidently we have

$$E = \frac{RT}{2F_v}\log K - \frac{RT}{2F_v}\log\frac{[HCl]^2}{p_{H_2}p_{Cl_2}}, \qquad (16)$$

where $$K = \left[\frac{[HCl]^2}{p_{H_2}p_{Cl_2}}\right]_e \text{ at equilibrium.}$$

The reaction may however be considered from a somewhat different point of view. If we assume that 0.1 M HCl is 83 per cent dissociated, we may describe the process as follows:

$$H_2 + Cl_2 \rightarrow 2\overset{+}{H} + 2\overset{-}{Cl}\ (c = 0.083); \quad \text{E.M.F.} = E \text{ volts.}$$

$$H_2, \underset{c = 0.083}{\overset{+}{H}, \overset{-}{Cl}}, Cl_2; \quad \text{E.M.F.} = E \text{ volts.} \qquad (17)$$

In this case we shall obtain

$$E = \frac{RT}{2F_v}\log K' - \frac{RT}{2F_v}\log\frac{[\overset{+}{H}]^2\,[\overset{-}{Cl}]^2}{p_{H_2}p_{Cl_2}}, \qquad (18)$$

where $K' = \dfrac{[\overset{+}{H}]^2\,[\overset{-}{Cl}]^2}{p_{H_2}p_{Cl_2}}$ at equilibrium. Since $\dfrac{[\overset{+}{H}] \times [\overset{-}{Cl}]}{[HCl]}$ is a constant (assuming the law of mass action) it is clear that equation (18) is identical with (16).

We may also consider in this case the process at each electrode and write

$$\left.\begin{aligned} H_2 + 2F_v &= 2\overset{+}{H}\ (c = 0.083); \quad E_1. \\ Cl_2 - 2F_v &= 2\overset{-}{Cl}\ (c = 0.083); \quad E_2. \end{aligned}\right\} \qquad (19)$$

Then we have

$$\left.\begin{aligned} E_1 &= \frac{RT}{2F_v}\log K_1 - \frac{RT}{2F_v}\log\frac{[\overset{+}{H}]^2}{p_{H_2}} \\ E_2 &= \frac{RT}{2F_v}\log K_2 - \frac{RT}{2F_v}\log\frac{[\overset{-}{Cl}]^2}{p_{Cl_2}} \end{aligned}\right\} \qquad (20)$$

and therefore, since $E = E_1 + E_2$,

$$E = \frac{RT}{2F_v}\log K_1K_2 - \frac{RT}{2F_v}\log\frac{[\overset{+}{H}]^2\,[\overset{-}{Cl}]^2}{p_{H_2}p_{Cl_2}}, \qquad (21)$$

identical with equation (18), since $K_1K_2 = K'$.

E.M.F. Under Normal Conditions

If in any reaction under consideration, the partial pressures of the gases are all equal to one atmosphere and the concentrations of the dissolved substances are all unity, i.e., one mole per liter, the E.M.F. under these conditions will be called the normal E.M.F. and be represented by the symbol $E°$. According to equation (11), we shall have

$$E° = \frac{RT}{nF_v} \log K, \tag{22}$$

and therefore in general

$$E = E° - \frac{RT}{nF_v}\left[\sum \nu_1 \log c_1 + \sum \nu_1 \log p_1\right]. \tag{23}$$

We shall apply the same considerations to the process at each electrode. Accordingly equation (13) will become

$$E = E° - \frac{RT}{2F_v} \log \frac{[\overset{++}{\text{Zn}}]}{[\overset{++}{\text{Cu}}]}, \tag{23a}$$

and equation (20) for a hydrogen electrode becomes

$$E = E° - \frac{RT}{2F_v} \log \frac{[\overset{+}{\text{H}}]^2}{p_{\text{H}_2}} = E° - \frac{RT}{F_v} \log \frac{[\overset{+}{\text{H}}]}{p_{\text{H}_2}^{\frac{1}{2}}}. \tag{24}$$

Single Electrode Potentials

It has not been found possible to measure satisfactorily the difference in potential between an electrode and a solution. For most purposes, it is unnecessary to know the absolute value of a single potential difference, since the E.M.F. of a combination is usually the difference of two electrode potentials, plus some liquid junction potentials. It will therefore be sufficient to assume a definite value for a certain single electrode potential in order to determine the values for all others. To illustrate this point by an analogy: the flow of heat along a conductor joining two bodies is determined by the difference in their temperatures and this difference on an absolute scale, say $T_2 - T_1$, is the same as the difference measured on any arbitrary scale, say the Centi-

grade scale where the zero point is defined in a perfectly arbitrary manner; i.e., $T_2 - T_1 = t_2 - t_1$, where t represents a Centigrade temperature.

Standard Electrodes

Two electrodes are widely used as standards, the normal calomel and the hydrogen electrode. In the first case, the potential difference in the combination $\mathrm{Hg,HgCl} - \underset{c=1}{\mathrm{KCl}}, - \underset{c=0.1}{\mathrm{KCl}}$ is placed equal to zero; in the second case, the potential of the half-cell $\underset{1\ \mathrm{atm.}}{\mathrm{H_2}} - \underset{c=1}{\overset{+}{\mathrm{H}}}$ is set equal to zero. This latter case requires fuller consideration. According to equation (24), adopting the hydrogen electrode as a standard is equivalent to setting $E° = 0$, so that the expression for any hydrogen electrode becomes

$$E = -\frac{RT}{F_y} \log \frac{[\overset{+}{\mathrm{H}}]}{p_{\mathrm{H_2}}^{\frac{1}{2}}}$$

or, if $p = 1$ atmosphere,

$$E = -\frac{RT}{F_y} \log [\overset{+}{\mathrm{H}}]. \qquad (25)$$

Now the equations we have developed hold accurately only for ideal gases or substances in very dilute solutions. They become exact if in place of the actual concentrations we substitute the activities as defined in Chap. XVI by equation (9) and the statement immediately following it. The strict definition of the standard hydrogen electrode is that it consists of hydrogen at one atmosphere in contact with a solution in which the activity of the hydrogen ions is unity. If we represent the activity of hydrogen ions by a, we shall have instead of (25)

$$E = -\frac{RT}{F_y} \log a. \qquad (26)$$

Thus suppose we have the combination in which the hydrogen gas is at atmospheric pressure, $\mathrm{H_2} - \underset{a_1}{\overset{c_1}{\overset{+}{\mathrm{H}}}} \Big\| \underset{a_2}{\overset{c_2}{\overset{+}{\mathrm{H}}}} - \mathrm{H_2}$, in which c_1 and c_2 are the concentrations and a_1 and a_2 the activities of the hydro-

gen ions and let us suppose that c_1 is very small, so that we can set $c_1 = a_1$. If E is the measured E.M.F. of this cell, then

$$E = \frac{RT}{F_\nu} \log \frac{a_2}{a_1} = \frac{RT}{F_\nu} \log \frac{a_2}{c_1}, \tag{27}$$

so that from known values of E and c_1, the activity a_2 of hydrogen ions of concentration c_2 can be calculated. Evidently we may also define the standard hydrogen electrode in the following way: it consists at any temperature of hydrogen at atmosphere pressure in contact with a solution in which the activity of the hydrogen ions is n times as great as in a solution in which the concentration of hydrogen ions is $\frac{1}{n}$, where n is a large number.* For most purposes, as a first approximation, we shall consider the activity of the ions to be equal to their concentration, but the reader should always bear in mind the character of the assumptions made. In this case it is equivalent to assuming that the laws of ideal gases hold for actual gases and for dissolved substances.

As further illustrations of expressions for single electrode potentials, we may consider the following reactions which take place at electrodes when a current flows:

(a) $\mathrm{Ag} + F_\nu = \overset{+}{\mathrm{Ag}}$. (b) $2\,\overset{-}{\mathrm{Cl}} + 2F_\nu = \mathrm{Cl_2}$. (c) $\overset{++}{\mathrm{Fe}} + F_\nu = \overset{+++}{\mathrm{Fe}}$.

(d) $\mathrm{Br_2} + 6\,\mathrm{H_2O} + 10\,F_\nu = 2\,\overset{-}{\mathrm{BrO_3}} + 12\,\overset{+}{\mathrm{H}}$.

The corresponding expressions for the single electrode potentials will be

$$\text{(a)}\quad E = E^\circ - \frac{RT}{F_\nu} \log [\overset{+}{\mathrm{Ag}}]. \tag{27a}$$

$$\text{(b)}\quad E = E^\circ - \frac{RT}{2F_\nu} \log \frac{p_{\mathrm{Cl_2}}}{[\overset{-}{\mathrm{Cl}}]^2}. \tag{27b}$$

$$\text{(c)}\quad E = E^\circ - \frac{RT}{F_\nu} \log \frac{[\overset{+++}{\mathrm{Fe}}]}{[\overset{++}{\mathrm{Fe}}]}. \tag{27c}$$

$$\text{(d)}\quad E = E^\circ - \frac{RT}{10F_\nu} \log \frac{[\overset{-}{\mathrm{BrO_3}}]^2\,[\overset{+}{\mathrm{H}}]^{12}}{[\mathrm{Br_2}]}. \tag{27d}$$

* Lewis, G. N., J. Amer. Chem. Soc., **35**, 25, (1913).

Comparison of Standard Electrodes

Following the practice of G. N. Lewis,* we shall define the normal calomel electrode as the combination Hg, HgCl, KCl (1.0 *M*), KCl, (0.1 *M*), designated by the symbols N. E. At 25° C, we have according to G. N. Lewis

$$H_2, \overset{+}{H}\ (M) \parallel \text{N. E.}; \quad E = 0.2828, \tag{28}$$

in which $H_2, \overset{+}{H}\ (M)$ represents the normal hydrogen electrode, in which the activity of hydrogen-ion is unity. According to the conventions we have adopted, the potential of the normal calomel electrode is −0.2828 when that of the normal hydrogen electrode is taken as zero. From the same article by G. N. Lewis *et al* cited above, we have, at 25° C.,

$$\text{Hg, HgCl} - \text{KCl (0.1 } M\text{), N. E.}; \quad E = -0.0529, \tag{28a}$$

giving the potential difference between the tenth-normal and the normal calomel electrodes.

Standard Cells

The usual method of determining the E.M.F. of any cell is to compare it with that of some standard cell, whose E.M.F. is known with sufficient accuracy. The cadmium cell is at the present time the standard which is generally used. This combination may be represented as follows: Cd (12.5 per cent amalgam), Hg_2SO_4, $CdSO_4 \cdot \frac{8}{3} H_2O$, Hg_2SO_4, Hg. The E.M.F. of this cell at 20° C., is 1.0183 volts, the pure mercury forming the positive pole. The Clark cell, formerly used extensively, differs from the cadmium cell in having zinc instead of cadmium and zinc sulphate instead of cadmium sulphate solution. The relation between the E.M.F.'s of the cadmium and Clark cells and the temperature can be represented by the following equations:

Cadmium Cell, $E_t = 1.0183 - 3.8 \times 10^{-5}\,(t - 20)$.

Clark Cell $E_t = 1.4325 - 1.19 \times 10^{-3}\,(t - 15) - 0.7 \times 10^{-5}\,(t - 15)^2$.

* J. Amer. Chem. Soc., **39**, 2255, (1917).

For details as to the experimental methods employed in measuring electromotive forces, textbooks of physical chemistry or of electrochemistry must be consulted.

Numerical Value of R

In order that in the equations given above the electromotive force shall be expressed in volts, it is evidently necessary that RT shall be expressed in volt-coulombs or joules. Now the value of R (the constant for one mole of an ideal gas) is evidently $\frac{pV}{T}$ and in order to obtain the value of R for use in electrochemical equations we must find the value of $\frac{pV}{T}$ in joules per degree. Now when $T = 273$, and $p = 1$ atmosphere, $V = 22{,}412$ cc. But 1 atmosphere is equal to $1{,}013{,}250 \frac{\text{dynes}}{\text{cm}^2}$; hence

$$R = \frac{pV}{T} = 83.16 \times 10^6 \frac{\text{ergs}}{\text{degree}} = 8.316 \frac{\text{joules}}{\text{degree}}.$$

Also since one faraday, $F_v = 96{,}500$ coulombs, the value of $\frac{R}{F_v}$ is $8.617 \times 10^{-5} \frac{\text{volts}}{\text{degree}}$. In most electrochemical equations, e.g., equation (24), the expression $\frac{R}{F_v}$ appears multiplying a natural logarithm. If however we desire to use ordinary logarithms in our equations, we must divide $\frac{R}{F_v}$ by the modulus 0.4343, thus obtaining the value

$$\frac{R}{0.4343\, F_v} = 1.984 \times 10^{-4} \frac{\text{volts}}{\text{degree}}.$$

It may be of use to tabulate the values of $\frac{RT}{0.4343\, F_v}$ for a number of temperatures.

TABLE XXIII. Values of $\frac{RT}{0.4343\, F_v}$

$t = 15°$	$T = 288$	0.05715
$t = 18°$	$T = 291$	0.05774
$t = 20°$	$T = 293$	0.05814
$t = 25°$	$T = 298$	0.05913
$t = 30°$	$T = 303$	0.06011

Concentration Cells

We shall take as our first example the following combination, arranged so that $c_1 > c_2$:

Zinc amalgam (conc. = c_1), $ZnSO_4$ solution,
Zinc amalgam (conc. = c_2).

When this cell functions, we shall have zinc going into the aqueous solution at one electrode and the same quantity of zinc being deposited at the other electrode. There is no change in the quantity of $ZnSO_4$ or of mercury; we can say that a certain quantity of zinc has been transferred isothermally and reversibly from an amalgam in which its concentration is c_1 to an amalgam in which its concentration is c_2. Let us calculate the affinity of this reversible process. In Chap. XV, it was shown that the expressions found for the thermodynamic functions of an ideal gas hold for substances in sufficiently dilute solution. Accordingly the thermodynamic potential at constant temperature of a mole of zinc dissolved in mercury is given by the equation

$$d\Phi = V\,dP, \tag{29}$$

where V is the volume of the amalgam containing one mole of zinc and P is the osmotic pressure of the zinc. Since $PV = RT$, we have

$$d\Phi = RT\,d\log_e P. \tag{30}$$

Hence the difference in the thermodynamic potential of a mole of zinc at osmotic pressures P_1 and P_2, is

$$\Phi_1 - \Phi_2 = RT\log_e \frac{P_1}{P_2}.$$

Since $P = cRT$, we may write, where A is the affinity of the process, E the E.M.F. of the combination and nF_v the quantity of electricity corresponding to the transfer of one mole of dissolved zinc,

$$nF_vE = A = \Phi_1 - \Phi_2 = RT\log_e \frac{c_1}{c_2}. \tag{31}$$

$$E = \frac{RT}{nF_v}\log_e \frac{c_1}{c_2} = \frac{0.0001984\,T}{n}\log_{10} \frac{c_1}{c_2}. \tag{32}$$

The value of n depends on the molecular weight of zinc dissolved in mercury. On the basis of results obtained by vapor-pressure measurements, we may give the formula Zn to the dissolved zinc; hence $n = 2$ and we obtain

$$E = 0.0000992\ T \log_{10} \frac{c_1}{c_2}. \qquad (33)$$

The calculation may be made in a somewhat different manner. Since according to equation (4), $nF_vE = A = W - p(V_2 - V_1) = \Phi_1 - \Phi_2$ and since in the cell considered the volume changes are negligible, we may set $nF_vE = A$ equal to W, the maximum work obtained in the process. According to equation (27) Chap. V, the maximum work obtainable when one mole of a gas goes from p_1 to p_2 is

$$RT \log_e \frac{p_1}{p_2} = RT \log_e \frac{c_1}{c_2},$$

where c_1 and c_2 are the corresponding concentrations. This gives us the same result as before. The validity of formula (33) is shown in the following table.

TABLE XXIV. ZINC AMALGAM AND $ZnSO_4$ SOLUTION

Temp., °C.	c_1	c_2	E obs.	E calc.
11.6	0.003366	0.00011305	0.0419	0.0416
18.0	0.003366	0.00011305	0.0433	0.0425
12.4	0.002280	0.0000608	0.0474	0.0446
60.0	0.002280	0.0000608	0.0520	0.0520

The experimental work was done by G. Meyer.* The results of Table XXIV may be taken as additional evidence that in dilute amalgams, the zinc molecule is monatomic. It may be mentioned that similar results have been obtained in the case of other metals, e.g. cadmium and copper.

We may next consider the following type of cell:

$$H_2\ (p_1\ \text{atm.}) - H_2SO_4 - H_2\ (p_2\ \text{atm.}). \qquad (34)$$

Gas electrodes (such as hydrogen, oxygen, chlorine electrodes) may be experimentally realized by having platinized platinum

* Zeit. f. physik. Chem., **7**, 447 (1891).

electrodes surrounded by the gas in question and immersed in the appropriate solution. Under these circumstances the passage of the gas into the ionic state occurs reversibly. The process that occurs in the cell just described consists essentially in converting hydrogen at p_1 atmospheres into hydrogen at p_2 atmospheres. The solution is not changed at all in amount or in concentration. The affinity of this process per mole of hydrogen transferred is evidently $RT \log_e \frac{p_1}{p_2}$. Since this process as carried out in the cell corresponds to the passage of $2 F_v$, ($H_2 + 2 F_v = 2 \overset{+}{H}$) we have

$$E = \frac{RT}{2 F_v} \log_e \frac{p_1}{p_2}. \qquad (35)$$

If p_1 is greater than p_2, the E.M.F. is positive and hence the positive current goes through the cell from left to right. If we have a similar cell, except that Cl_2 takes the place of H_2 and some chloride the place of the H_2SO_4, we shall have as the affinity of the process per mole of chlorine transferred $RT \log_e \frac{p_1}{p_2}$. But since the process at the electrodes may be represented as follows: $Cl_2 - 2 F_v = 2 \overset{-}{Cl}$ or $2 \overset{-}{Cl} + 2 F_v = Cl_2$, the direction of the current will be opposite to that of the hydrogen cell. This may be represented by the following scheme:

$$Cl_2\ (p_1 \text{ atm.}),\ HCl,\ Cl_2\ (p_2 \text{ atm.});\ E = -\frac{RT}{2 F_v} \log_e \frac{p_1}{p_2}. \qquad (36)$$

We may now consider cells in which the electrodes are identical but are in contact with solutions of different concentrations. We shall provisionally omit consideration of the liquid junction potentials. The following cells may be taken as typical:

(a) $\underset{}{Ag},\ \underset{c_1}{AgNO_3} \parallel \underset{c_2}{AgNO_3},\ Ag.$

(b) $\underset{}{Tl},\ \underset{c_1}{Tl_2SO_4} \parallel \underset{c_2}{Tl_2SO_4},\ Tl.$

(c) $\underset{}{Ag},\ \underset{\text{(solid)}}{AgCl},\ \underset{c_1}{KCl} \parallel \underset{}{KNO_3} \parallel \underset{c_2}{AgNO_3},\ Ag.$

(d) $\underset{}{H_2},\ \underset{c_1}{NaOH} \parallel \underset{c_2}{HCl},\ H_2.$

(e) $\underset{}{Zn},\ \underset{c_1}{ZnSO_4} \parallel \underset{c_2}{ZnSO_4},\ Zn.$

In each of the above cells, let α_1 and α_2 be the degrees of dissociation corresponding to the concentrations c_1 and c_2. According to our convention, an electrode potential is considered positive if there is tendency for the positive current to go from the electrode into the solution. According to equation (27a), the potential of the silver electrode on the left in combination "a" is

$$E_1 = E^\circ - \frac{RT}{F_y} \log_e (\alpha_1 c_1);$$

the potential of the right hand electrode is

$$E_2 = E^\circ - \frac{RT}{F_y} \log_e (\alpha_2 c_2).$$

Hence the E.M.F. of combination "a" omitting the liquid junction potential is

$$E = E_1 - E_2 = \frac{RT}{F_y} \log_e \frac{\alpha_2 c_2}{\alpha_1 c_1} = \frac{RT}{F_y} \log_e \frac{[\overset{+}{\mathrm{Ag}}]_2}{[\overset{+}{\mathrm{Ag}}]_1} \quad \text{(cell a)}. \quad (37)$$

If $\alpha_2 c_2$ is greater than $\alpha_1 c_1$, that is, if c_2 is greater than c_1, the value of E is positive and the current will flow from left to right in the cell, from the dilute to the more concentrated solution. According to Table XXIII, at 25° C., the E.M.F. of such a cell will be

$$E = 0.0591 \log_{10} \frac{[\overset{+}{\mathrm{Ag}}]_2}{[\overset{+}{\mathrm{Ag}}]_1} \quad \text{(cell a)}. \quad (38)$$

Similarly the E.M.F. of cell "b" will be

$$E = \frac{RT}{2F_y} \log_e \left(\frac{2\alpha_2 c_2}{2\alpha_1 c_1}\right)^2 = \frac{RT}{F_y} \log_e \frac{\alpha_2 c_2}{\alpha_1 c_1} = \frac{RT}{F_y} \log_e \frac{[\overset{+}{\mathrm{Tl}}]_2}{[\overset{+}{\mathrm{Tl}}]_1}. \quad (39)$$

In the case of cell "e", we shall have

$$E = \frac{RT}{2F_y} \log \frac{\alpha_2 c_2}{\alpha_1 c_1} = \frac{RT}{2F_y} \log \frac{[\overset{++}{\mathrm{Zn}}]_2}{[\overset{++}{\mathrm{Zn}}]_1}. \quad (40)$$

At 25° C., the E.M.F. of cell "e" will be

$$E = 0.0296 \log_{10} \frac{[\overset{++}{\mathrm{Zn}}]_2}{[\overset{++}{\mathrm{Zn}}]_1}. \quad (41)$$

The E.M.F. of combination "c" will be given by the expression

$$E = \frac{RT}{F_y} \log_e \frac{[\overset{+}{\text{Ag}}]_2}{[\overset{+}{\text{Ag}}]_1},$$

but the value of $[\overset{+}{\text{Ag}}]_1$ will depend on the solubility of AgCl in KCl of concentration c_1. Assuming that K is the solubility product for AgCl, where $K = [\overset{+}{\text{Ag}}]_1 \times [\overset{-}{\text{Cl}}]$, then since $[\overset{-}{\text{Cl}}] = \alpha_1 c_1$, we have

$$[\overset{+}{\text{Ag}}]_1 = \frac{K}{\alpha_1 c_1}.$$

Hence the E.M.F. of this cell becomes

$$E = \frac{RT}{F_y} \log_e \frac{\alpha_2 c_2 \times \alpha_1 c_1}{K}. \qquad (42)$$

Taking $K = 1.99 \times 10^{-10}$ at 25° C. and assuming $c_1 = c_2 = 0.1$ and $\alpha_1 = 0.85$ and $\alpha_2 = 0.82$, we obtain at 25° C.,

$$E = 0.0591 \log_{10} \frac{0.082 \times 0.085}{1.99 \times 10^{-10}} = 0.446 \text{ volts},$$

whereas the value experimentally found by Goodwin was 0.45 volts. Coming finally to the combination (d) we see that this may be looked on as a hydrogen concentration cell and the E.M.F. will be

$$E = \frac{RT}{F_y} \log_e \frac{[\overset{+}{\text{H}}]_2}{[\overset{+}{\text{H}}]_1}.$$

Assuming the acid and base to be at normal concentration and to be 80 per cent dissociated, we shall have $[\overset{+}{\text{H}}]_2 = 0.8$. If K_w is the dissociation constant for water, we shall have $[\overset{+}{\text{H}}]_1 \times [\overset{-}{\text{OH}}] = [\overset{+}{\text{H}}]_1 \times 0.8 = K_w$. Hence at 18° C., the cell will have the following E.M.F., if we eliminate the liquid junction potential which is in this case appreciable:

$$E = 0.0577 \log_{10} \frac{0.8 \times 0.8}{K_w}.$$

According to Nernst,* the value of E at 18° C. is 0.81 volt.

Accordingly $$0.81 = 0.0577 \log_{10} \frac{0.8 \times 0.8}{K_w},$$

and hence $K_w = 0.64 \times 10^{-14}$ at 18° C. in close agreement with values obtained by other methods.

Liquid Junction Potentials

The calculation of the potential difference at the boundary of two liquids is in general rather difficult; we shall confine ourselves to cases in which the task is comparatively easy. For the combination

$$\mathrm{Ag}, \quad \underset{c_1}{\mathrm{AgNO_3}}, \quad \underset{c_2}{\mathrm{AgNO_3}}, \quad \mathrm{Ag}$$

we have already calculated (equation (37)) the E.M.F. due to the two electrode potentials. We shall now proceed to determine the potential difference at the boundary of the two liquids, $\underset{c_1}{\mathrm{AgNO_3}}$ and $\underset{c_2}{\mathrm{AgNO_3}}$. According to our convention, a positive value for this E.M.F. will mean that positive electricity tends to flow across the boundary from left to right. Let n_c and n_a be the transference numbers of the cation and anion respectively and let us suppose that one faraday of positive electricity flows across the boundary from left to right. Then n_c equivalents of $\overset{+}{\mathrm{Ag}}$ will pass the boundary from left to right and n_a equivalents of $\overset{-}{\mathrm{NO_3}}$ will go in the opposite direction. If α_1 and α_2 are the degrees of dissociation corresponding to c_1 and c_2, the affinity of the process just described will be equal to the decrease in the thermodynamic potential, or according to equations (30), (31) and (32),

$$F_v E_1 = A = \Phi_1 - \Phi_2 = n_c RT \log_e \frac{\alpha_1 c_1}{\alpha_2 c_2} + n_a RT \log_e \frac{\alpha_2 c_2}{\alpha_1 c_1}. \quad (43)$$

Bearing in mind that $n_a + n_c = 1$, we have for E_1, the liquid junction potential

$$E_1 = (n_a - n_c) \frac{RT}{F_v} \log_e \frac{\alpha_2 c_2}{\alpha_1 c_1} = (2\, n_a - 1) \frac{RT}{F_v} \log_e \frac{\alpha_2 c_2}{\alpha_1 c_1}. \quad (44)$$

* Zeit. f. physik. Chem. **14**, 155 (1894).

Evidently in this case the liquid junction potential will vanish if $n_a = n_c = 0.5$. The total E.M.F. for the combination Ag, $\underset{c_1}{AgNO_3}$, $\underset{c_2}{AgNO_3}$, Ag is the sum of the E.M.F.'s given by (44) and (37), i.e.,

$$E = 2\, n_a \frac{RT}{F_y} \log_e \frac{\alpha_2 c_2}{\alpha_1 c_1}. \tag{45}$$

Equation (45) will give the total E.M.F. in any concentration cell of the kind considered: that is, one in which the electrolyte is of the uni-univalent type and the electrodes furnish positive ions. If the electrodes furnish negative ions, then the total E.M.F. will be

$$E = -2\, n_c \frac{RT}{F_y} \log_e \frac{\alpha_2 c_2}{\alpha_1 c_1}, \tag{46}$$

as in the cell

$$\underset{1\text{ atm.}}{Cl_2}, \quad \underset{c_1}{NaCl}, \quad \underset{c_2}{NaCl}, \quad \underset{1\text{ atm.}}{Cl_2}.$$

We may now calculate in a more general way the potential difference at the boundary of two solutions of the same electrolyte but at different concentrations. It may be well to state explicitly the assumptions underlying the calculation. We assume (1) that the electrolyte dissociates into two kinds of ions only, so that there are no intermediate ions; e.g., we assume that a salt like $Pb(NO_3)_2$ forms only the ions $\overset{++}{Pb}$ and $\overset{-}{NO_3}$; (2) that the activities of the ions are equal to their concentrations; (3) that the transference numbers are independent of the concentrations considered. Let us consider the following case:

$$\underset{c_1}{A_xB_y}, \quad \underset{c_2}{A_xB_y}, \tag{47}$$

where N_c and N_a are the valences of the positive radical A and negative radical B respectively and where n_c and n_a are the transference numbers. If one faraday of positive electricity passes the boundary from solution c_1 to solution c_2, we shall have $\frac{n_c}{N_c}$ moles of the ion A going from a concentration $x\alpha_1 c_1$ to a concentration $x\alpha_2 c_2$ and $\frac{n_a}{N_a}$ moles of the ion B, going from a concentra-

tion $y\alpha_2 c_2$ to a concentration $y\alpha_1 c_1$. The affinity of this process is evidently $\frac{n_c}{N_c} RT \log_e \frac{\alpha_1 c_1}{\alpha_2 c_2} + \frac{n_a}{N_a} RT \log_e \frac{\alpha_2 c_2}{\alpha_1 c_1} = F_y E_l$ where E_l is the liquid potential from left to right. We therefore obtain for the value of E_l,

$$E_l = \left(\frac{n_a}{N_a} - \frac{n_c}{N_c}\right) \frac{RT}{F_y} \log_e \frac{\alpha_2 c_2}{\alpha_1 c_1}, \tag{48}$$

expressing the tendency for positive electricity to go from c_1 to c_2.

In the case of the cell, Tl, $\underset{c_1}{Tl_2SO_4}$, $\underset{c_2}{Tl_2SO_4}$, Tl, $N_c = 1$, $N_a = 2$, hence

$$E_l = \left(\frac{3\,n_a - 2}{2}\right) \frac{RT}{F_y} \log_e \left(\frac{\alpha_2 c_2}{\alpha_1 c_1}\right).$$

Combining this with expression (39) we obtain for the total E.M.F. of the concentration cell

$$E = \frac{3\,n_a}{2} \frac{RT}{F_y} \log_e \frac{[Tl]_2^+}{[Tl]_1^+}. \tag{49}$$

Applying similar considerations to the concentration cell, Zn, $\underset{c_1}{ZnCl_2}$, $\underset{c_2}{ZnCl_2}$, Zn, we obtain

$$E_l = \left(\frac{n_a}{1} - \frac{n_c}{2}\right) \frac{RT}{F_y} \log_e \frac{[Zn]_2^{++}}{[Zn]_1^{++}} = \left(\frac{3\,n_a - 1}{2}\right) \frac{RT}{F_y} \log_e \frac{[Zn]_2^{++}}{[Zn]_1^{++}}.$$

The two electrode potentials would give the E.M.F.

$$\frac{RT}{2F_y} \log_e \frac{[Zn]_2^{++}}{[Zn]_1^{++}},$$

so that in this case the total E.M.F. would be

$$E = \frac{3\,n_a}{2} \frac{RT}{F_y} \log_e \frac{[Zn]_2^{++}}{[Zn]_1^{++}}. \tag{50}$$

So far we have been considering the potential difference at the boundary of two solutions of the same electrolyte. For the general case in which the two solutions may contain any number of different electrolytes at any concentrations, the problem of

calculating the difference of potential becomes rather difficult. The reader is referred to the following investigators for information: Planck,* Johnson,† Henderson,‡ Bjerrum § and Lewis ||. We shall consider only the rather simple case in which the two solutions have the same concentration. We also suppose that each solution contains but one electrolyte and that the two electrolytes have a common ion. The two electrolytes are also supposed to be completely ionized or at least to have equal degrees of ionization and the ions are supposed to be univalent. We may take the combination HCl, KCl as a type. If U_1, U_2 and V are the mobilities of $\overset{+}{H}$, $\overset{+}{K}$ and $\overset{-}{Cl}$ respectively, the potential difference according to both Planck and Henderson is

$$E = \frac{RT}{F_v} \log_e \frac{U_1 + V}{U_2 + V}. \tag{51}$$

If this is positive, it means that there is a tendency for the positive current to flow from left to right across the boundary. If λ_{01} and λ_{02} are the equivalent conductances at infinite dilution of the two electrolytes, then $U_1 + V = \lambda_{01}$ and $U_2 + V = \lambda_{02}$ and equation (51) becomes

$$E = \frac{RT}{F_v} \log_e \frac{\lambda_{01}}{\lambda_{02}}. \tag{52}$$

This assumes that the mobilities of the ions do not change with change in concentration. If the two electrolytes have the same degree of dissociation, $\frac{\lambda_1}{\lambda_2} = \frac{\lambda_{01}}{\lambda_{02}}$, where λ_1 and λ_2 are the equivalent conductances at the given concentration. Lewis and Sargent in the article cited above give reasons for believing that the following expression should hold more accurately than equation (52); viz.:

$$E = \frac{RT}{F_v} \log_e \frac{\lambda_1}{\lambda_2}. \tag{53}$$

* Wied. Ann. **40,** 561 (1890).
† Ann. der Physik. **14,** 995 (1904).
‡ Zeit. f. physik. Chem. **59,** 118 (1907); **63,** 325 (1908).
§ Zeit. f. Elektrochemie **17,** 391 (1911).
|| J. Amer. Chem. Soc. **31,** 363 (1909).

Concentration Double-Cells

As a typical example of a concentration double-cell, we may consider the following combination,

$$\underset{c_1}{\mathrm{ZnCl_2}},\ \underset{\text{solid}}{\mathrm{HgCl}},\ \mathrm{Hg},\ \underset{\text{solid}}{\mathrm{HgCl}},\ \underset{c_2}{\mathrm{ZnCl_2}},$$

which may be looked on as consisting of two cells of the type, $Zn, ZnCl_2, HgCl, Hg$ arranged so as to oppose each other. The E.M.F. of the double-cell can be easily calculated, the usual assumptions in regard to the dissociation of the salts and the activities of the ions being made. The sole result of sending two faradays of electricity through the combination is the formation of a mole of $\overset{++}{Zn}$ and two moles of $\overset{-}{Cl}$ in the solution of concentration c_1, and the disappearance of a mole of $\overset{++}{Zn}$ and two moles of $\overset{-}{Cl}$ from the solution of concentration c_2. The amount and state of metallic zinc, mercury and HgCl do not change in the least. Since three moles (one of $\overset{++}{Zn}$ and two of $\overset{-}{Cl}$) go from concentration $\alpha_2 c_2$ (or $2\,\alpha_2 c_2$) to $\alpha_1 c_1$ (or $2\,\alpha_1 c_1$) the decrease in the thermodynamic potential is $3\,RT \log_e \frac{\alpha_2 c_2}{\alpha_1 c_1}$ and hence the E.M.F. of the double cell is

$$E = \frac{3\,RT}{2\,F_y} \log_e \frac{\alpha_2 c_2}{\alpha_1 c_1} = \frac{3\,RT}{2\,F_y} \log_e \frac{[\overset{++}{Zn}]_2}{[\overset{++}{Zn}]_1}. \qquad (54)$$

The formula (54) can easily be extended to cover the general case. Evidently the combination $HgCl - Hg - HgCl$ could be replaced by any other arrangement which would furnish or take up chloride ions (e.g. $AgCl - Ag - AgCl$), provided no appreciable amount of the chloride ions is furnished by anything but the zinc chloride.

Chemical Cells

When concentration cells are functioning, the principal change that occurs is that some substance or substances are transferred from a region in which they have a certain concentration to a region in which they have a different concentration. There is in general nothing that could be described as a chemical

change, that is, a transformation of some substances into different substances. We shall now consider cells in which chemical changes play an important part and we may illustrate this case by considering first of all the Daniell Cell,

$$\mathrm{Zn},\quad \underset{c_1}{\mathrm{ZnSO_4}} \;\Big\|\; \underset{c_2}{\mathrm{CuSO_4}},\quad \mathrm{Cu}, \tag{55}$$

in which the liquid junction potential is supposed to be eliminated. If E°_{Zn} and E°_{Cu} represent the normal single electrode potentials and if $[\overset{++}{Zn}]$ and $[\overset{++}{Cu}]$ are the concentrations of zinc ions and copper ions, then (in harmony with equations (27a) to (27d)),

$$E_{Zn} = E^\circ_{Zn} - \frac{RT}{2F_y}\log_e[\overset{++}{Zn}] \quad \text{and} \quad E_{Cu} = E^\circ_{Cu} - \frac{RT}{2F_y}\log_e[\overset{++}{Cu}],$$

and the total E.M.F. of the Daniell Cell is

$$E = E_{Zn} - E_{Cu} = E^\circ_{Zn} - E^\circ_{Cu} - \frac{RT}{2F_y}\log_e\frac{[\overset{++}{Zn}]}{[\overset{++}{Cu}]}. \tag{56}$$

Comparing this with equations (23a) and (22) we see that $E^\circ_{Zn} - E^\circ_{Cu}$ is equal to

$$\frac{RT}{2F_y}\log K \quad \text{or} \quad \frac{RT}{2F_y}\log_e\frac{[\overset{++}{Zn}]_e}{[\overset{++}{Cu}]_e},$$

the subscript "e" indicating that $[\overset{++}{Zn}]_e$ and $[\overset{++}{Cu}]_e$ are concentrations at which the four substances, Zn, Cu, $\overset{++}{Zn}$ and $\overset{++}{Cu}$ are in equilibrium. Equation (56) gives also in a quantitative way the variation in the E.M.F. of a Daniell Cell with changes in the concentrations of the zinc and copper ions.

We may also consider a cell in which all the chemical changes that occur take place between substances in the solution, i.e., the actual electrodes suffer no change and serve only to conduct the electricity into and out of the solution. The following reaction may occur in a cell:

$$\mathrm{SnCl_2} + 2\,\mathrm{FeCl_3} \rightleftarrows \mathrm{SnCl_4} + 2\,\mathrm{FeCl_2},$$

or written ionically,

$$\overset{++}{\mathrm{Sn}} + 2\,\overset{+++}{\mathrm{Fe}} \rightleftarrows \overset{++++}{\mathrm{Sn}} + 2\,\overset{++}{\mathrm{Fe}}. \tag{57}$$

A cell in which this transformation will occur may be represented by the following scheme:

$$(\mathrm{Pt})\ \begin{matrix}\overset{++}{\mathrm{Sn}} \\ \overset{++++}{\phantom{\mathrm{Sn}}}{}' \\ \overset{++++}{\mathrm{Sn}}\end{matrix}\ \Big\|\ \begin{matrix}\overset{+++}{\mathrm{Fe}} \\ \overset{++}{\phantom{\mathrm{Fe}}}{}' \\ \overset{++}{\mathrm{Fe}}\end{matrix}\ ,\ (\mathrm{Pt}). \qquad (58)$$

According to (58) two platinum electrodes dip into different solutions, one containing stannous and stannic ions, the other ferrous and ferric ions. When the cell (58) functions, positive electricity will enter by one electrode and convert $\overset{++}{\mathrm{Sn}}$ into $\overset{++++}{\mathrm{Sn}}$; at the other electrode, $\overset{+++}{\mathrm{Fe}}$ will give up positive electricity to the electrode and be reduced to $\overset{++}{\mathrm{Fe}}$. The reaction represented by equation (57) corresponds to the passage of two faradays of electricity. According to equation (11), the E.M.F. of the cell (58) will be

$$E = \frac{RT}{2F_v}\log K - \frac{RT}{2F_v}\log_e \frac{[\overset{++++}{\mathrm{Sn}}]\,[\overset{++}{\mathrm{Fe}}]^2}{[\overset{++}{\mathrm{Sn}}]\,[\overset{+++}{\mathrm{Fe}}]^2}, \qquad (59)$$

where K is the value of $\dfrac{[\overset{++++}{\mathrm{Sn}}]\,[\overset{++}{\mathrm{Fe}}]^2}{[\overset{++}{\mathrm{Sn}}]\,[\overset{+++}{\mathrm{Fe}}]^2}$ when the four substances $\overset{++}{\mathrm{Sn}}$, $\overset{++++}{\mathrm{Sn}}$, $\overset{++}{\mathrm{Fe}}$ and $\overset{+++}{\mathrm{Fe}}$ are in equilibrium. Evidently, according to (59), the equilibrium constant of the reaction can be calculated from measurements of E if the ionic concentrations are known or, conversely, from a knowledge of the equilibrium constant of the reaction, the E.M.F. can be calculated as a function of the ionic concentrations.

Oxidation and Reduction

When a Daniell cell is functioning, metallic zinc is converted into zinc ions (or zinc sulphate) and copper ions (or copper sulphate) are reduced to metallic copper. We may make the general statement that oxidation occurs where the positive current enters and reduction where the positive current leaves the cell. From this point of view it may be said that chemical changes occur in all cells when functioning, even in concentration cells, although in this case the chemical changes at one electrode are exactly reversed at the other. We may characterize the chemical

changes that take place in the Daniell cell by saying that zinc is a stronger reducing agent than copper and hence the copper sulphate is reduced to copper and the zinc oxidized to zinc sulphate. We have in measurements of the E.M.F. of cells a means of comparing substances or solutions as to their reducing (or oxidizing) power. It is convenient to think of hydrogen under normal conditions as a standard reducer with which to compare other reducers. Now the reducing power of hydrogen or any other substance depends not only on the concentration of the reducer but also on that of the oxidation product. We may therefore take hydrogen at one atmosphere in contact with hydrogen ions at normal concentration as the standard reducing agent in the electro-chemical sense. Suppose we wish to compare the reducing power of metallic zinc with that of hydrogen; in order to give an accurate answer we must specify the concentration of the oxidation product of the zinc, viz.: zinc ions or some zinc salt. Thus we should make up the cell

$$\mathrm{Zn},\ \underset{c}{\overset{++}{\mathrm{Zn}}}\ \Big\|\ \underset{c=1}{\overset{+}{\mathrm{H}}},\ \mathrm{H_2}; \qquad \text{E.M.F.} = E \text{ volts.} \tag{60}$$

The E.M.F. of this cell is (see equation (27a))

$$E = E^\circ_{\mathrm{Zn}} - \frac{RT}{2F_y} \log_e [\overset{++}{\mathrm{Zn}}], \tag{61}$$

and this value is a measure of the reducing power of zinc in contact with zinc ions of the given concentration as compared with the reducing power of hydrogen in the normal hydrogen electrode. If E is positive, the combination is a better reducer and if it is negative, it is a poorer reducer than hydrogen. Moreover if E is positive, the combination is a poorer oxidizer and if it is negative, it is a better oxidizer than hydrogen ions. Thus the combination $\mathrm{H_2}$, $\overset{+}{\mathrm{H}}$ may be taken as a standard reducing or a standard oxidizing system. Hence if the single electrode potential for any combination expressed according to our conventions is positive, the combination is a better reducing agent than the normal hydrogen electrode and if the single electrode potential is negative, the combination is a stronger oxidizing agent.

An experimental test of equation (11) was made by Knüpffer * at the instance of Bredig in the case of a reaction in which the value of the equilibrium constant could be determined by chemical means. The process studied may be represented by the equation,

$$KSCN + \underset{\text{solid}}{TlCl} \rightleftarrows KCl + \underset{\text{solid}}{TlSCN}. \tag{62}$$

From the ionic point of view the reaction is:

$$\bar{S}CN + \underset{\text{solid}}{TlCl} \rightleftarrows \bar{Cl} + \underset{\text{solid}}{TlSCN}, \tag{63}$$

and the equilibrium constant may be expressed in the form

$$K_c = \frac{[KCl]_e}{[KSCN]_e} = \frac{[\bar{Cl}]_e}{[\bar{S}CN]_e}. \tag{64}$$

The affinity of the process depends only on the ratio of the concentrations of $\bar{Cl}$ and $\bar{S}CN$ since TlCl and TlSCN are both present as solids and $\overset{+}{K}$ takes no appreciable part in the reaction. The affinity of the process according to equation (11) is accordingly

$$A = RT \log_e K_c - RT \log_e \frac{[\bar{Cl}]}{[\bar{S}CN]}; \tag{65}$$

and if we represent the ratio $\frac{[\bar{Cl}]}{[\bar{S}CN]}$ by r, then

$$A = RT \log_e \frac{K_c}{r}.$$

The process may be carried out reversibly in the following cell:

$$\text{Tl-amalgam}, \underset{\text{solid}}{TlSCN}, KSCN \;\|\; KCl, \underset{\text{solid}}{TlCl}, \text{Tl-amalgam}. \tag{66}$$

A positive current flowing in this cell from left to right will be accompanied by the chemical changes represented in equations (62) or (63). In Table XXV will be found the values of the E.M.F. found experimentally and those calculated according to the following equation, readily deduced from equation (65):

$$E = \frac{RT}{F_v} \log_e \frac{K_c}{r}. \tag{67}$$

* Zeit. für physik. Chemie. **26,** 255 (1898).

TABLE XXV. E.M.F.

$t°$ C.	$r = \frac{[\bar{Cl}]}{[\bar{SCN}]}$	K_c observed	E observed	E calc.
0.8	0.84	1.74	+0.0175	+0.0172
0.8	1.55	1.74	+0.0037	+0.0027
20.0	0.84	1.24	+0.0105	+0.0098
20.0	1.52	1.24	−0.0048	−0.0051
39.9	0.83	0.85	+0.0010	+0.0006
39.9	1.50	0.85	−0.0141	−0.0153

The agreement between the observed and calculated values of the E.M.F. is very satisfactory. The cell just discussed may also be looked on as a concentration cell and its E.M.F. may be calculated from that point of view. The equilibrium constant

$$K_c = \frac{[\bar{Cl}]_e}{[\bar{SCN}]_e},$$

is also equal to

$$\frac{[\dot{Cl}]_e \times [\dot{Tl}]_e}{[\bar{SCN}]_e \times [\dot{Tl}]_e} = \frac{S_2}{S_1},$$

where S_1 and S_2 are the solubility products of TlSCN and TlCl. In the concentration cell,

$$[\dot{Tl}]_1 = \frac{S_1}{[\bar{SCN}]} \quad \text{and} \quad [\dot{Tl}]_2 = \frac{S_2}{[\bar{Cl}]},$$

and hence the E.M.F. of the cell is

$$E = \frac{RT}{F_v} \log \frac{[\dot{Tl}]_2}{[\dot{Tl}]_1} = \frac{RT}{F_v} \log \frac{S_2}{S_1} - \frac{RT}{F_v} \log \frac{[\bar{Cl}]}{[\bar{SCN}]},$$

and this is identical with equation (67).

In Table XXVI are collected a number of normal electrode potentials referred to the normal hydrogen electrode as already defined. A positive sign indicates that there is a tendency for positive electricity to go from the electrode into the solution. The temperature may usually be taken as 25° C.

TABLE XXVI. NORMAL ELECTRODE POTENTIALS

Concentration of dissolved substances = 1 mole per liter.
Pressure of gases = 1 atmosphere.

Lower state of oxidation	Higher state of oxidation	E° = normal single potential	Authority
Li	Li^+	3.022	Lewis and Keyes
Rb	Rb^+	2.922	Lewis and Argo
K	K^+	2.920	Lewis and Keyes
Na	Na^+	2.710	Lewis and Kraus
Mg	Mg^{++}	1.55	
$H_2 + 2\ OH^-$	$2\ H_2O$	0.83	
Zn	Zn^{++}	0.76	
Fe	Fe^{++}	0.42	
Cd	Cd^{++}	0.40	
Tl	Tl^+	0.334	Lewis and von Ende
Co	Co^{++}	0.29	
Ni	Ni^{++}	0.22	
Sn	Sn^{++}	0.14	Noyes
Pb	Pb^{++}	0.13	
H_2	$2\ H^+$	±0.000	
Cu	Cu^{++}	−0.34	Lewis and Lacey
Ag	Ag^+	−0.798	
Hg	Hg^{++}	−0.86	
$4\ OH^-$	$O_2 + 2\ H_2O$	−0.397	
$2\ I^-$	I_2 (solid)	−0.54	
Fe^{++}	Fe^{+++}	−0.75	
$2\ Br^-$	Br_2 (aqueous)	−1.087	
$2\ H_2O$	$O_2 + 4\ H^+$	−1.23	
$2\ Cl^-$	Cl_2 (gaseous)	−1.362	Lewis and Rupert
$2\ F^-$	F_2 (gaseous)	−1.9	

Applications of the Gibbs-Helmholtz Equation

According to equations (55a) and (57) of Chap. IX, the affinity of a process carried out at constant temperature and pressure is given by the expression

$$(\Phi_1 - \Phi_2)_{p,T} = A = H_p + T\left(\frac{dA}{dT}\right)_p. \tag{68}$$

If the affinity is expressed in terms of the electrical energy that the given process will furnish when it occurs in a cell, we have, since $A = nF_vE$,

$$E = \frac{H_p}{nF_v} + T\left(\frac{dE}{dT}\right)_p. \tag{69}$$

In this expression, H_p is the difference in the values of the heat-function, $U + pV$, in the initial and final states; it is therefore equal to the heat that would be evolved if the process took place without furnishing any electrical energy. Since H_p is usually expressed in calories and F_vE in volt-coulombs or joules, equation (69) will give E in volts if we divide the numerical value of the faraday (96,500) by 4.186. We thus obtain

$$E = \frac{H_p}{23053\,n} + T\left(\frac{dE}{dT}\right)_p. \tag{70}$$

Evidently the heat absorbed from the surroundings during the reversible process is equal to $nF_vT\left(\frac{dE}{dT}\right)_p$. In many concentration cells the sole result of the process which takes place in the cell is the transfer of some substance or substances (gases or dissolved substances) from a certain pressure or concentration to a lower pressure or concentration. If these substances may be considered either as ideal gases or as present in dilute solution, both the function U and the function pV will not change during the isothermal process and hence $H_p = U_1 - U_2 + p\,(V_1 - V_2)$ will be zero. When this is the case, according to equation (70),

$$E = T\left(\frac{dE}{dT}\right)_p,$$

and therefore

$$\frac{dE}{dT} = \frac{E}{T} \quad \text{and} \quad E = kT. \tag{71}$$

In other words the E.M.F. is proportional to the absolute temperature.

According to equation (68) or (69), the value of H_v for a process can be calculated if A and $\left(\frac{dA}{dT}\right)_v$ or E and $\left(\frac{dE}{dT}\right)_v$ are known. It is not in general possible to calculate A or E if only H_v is given. It is true that in many cases the term $T\left(\frac{dA}{dT}\right)_v$ or $T\left(\frac{dE}{dT}\right)_v$ is small compared with the other terms, so that sometimes the affinity is approximately equal to H_v or the electromotive force of a cell is equal to $\frac{H_v}{nF_v}$. But, as we just pointed out, in a certain class of concentration cells the value of H_v is negligible and

$$A = T\left(\frac{dA}{dT}\right)_v \quad \text{or} \quad E = T\left(\frac{dE}{dT}\right)_v.$$

We may apply the Gibbs-Helmholtz equation to the following cell:

Ag, AgCl (solid), KCl (0.1 M), KNO_3, (0.1 M), $AgNO_3$ (0.1 M), Ag.

When one faraday passes through this cell from left to right, the sole change of any importance is the precipitation of one mole of AgCl from solution. H_v will therefore be the heat of precipitation of AgCl which Thomsen finds to be 15,740 calories at 18° C. Lovén determined the E.M.F. of this cell to be 0.443 volts at 15° C., and 0.394 volts at 77° C. Assuming that the E.M.F. varies linearly with the temperature, we find $\frac{dE}{dT} = -0.00079$. At 18° C. we may take $E = 0.441$, $T\frac{dE}{dT} = 291 \times (-.00079) = -0.230$. Hence $H_v = 23{,}053 \times [0.441 + 0.230] = 15{,}470$ calories, in good agreement with Thomsen's value. Evidently the affinity of this process is $A = F_vE = 23{,}053 \times 0.441 = 10{,}170$ calories and the heat evolved during the reversible process is $-F_vT\frac{dE}{dT} = 23{,}053 \times 0.230 = 5300$ calories.

We may also apply the formula to the Daniell Cell

$$Zn, \quad ZnSO_4 + 100\ H_2O \parallel CuSO_4 + 100\ H_2O, \quad Cu,$$

for which we have the following data at 0° C.:

$$E = 1.0962 \text{ volts}; \frac{dE}{dT} = +0.000034;$$

H_p (determined thermochemically) = 50,110 calories. Hence $A = 2 \times 23{,}053 \times 1.0962 = 50{,}541$ calories and the heat evolved $= -2 \times 273 \times 23{,}053 \times 0.000034 = -428$ calories. Therefore H_p (calculated electrochemically) = 50,541 − 428 = 50,113 calories. Additional applications of the Gibbs-Helmholtz formula will be met with in the problems at the end of this Chapter.

The data in Tables XXVII to XXX are taken chiefly from the critical compilation of Noyes and Falk.*

TABLE XXVII. EQUIVALENT CONDUCTANCE λ AND CONDUCTANCE-VISCOSITY PRODUCT ($\lambda\eta$) AT 18° C.

$$\text{Concentration} = \frac{\text{equivalents}}{\text{liters}}.$$

Concentration		0	0.01	0.02	0.05	0.10	0.20	0.50	1.0
NaCl	λ	108.9	101.88	99.55	95.66	91.96	87.67	80.89	74.31
	$\lambda\eta$	108.9	101.97	99.73	96.10	92.75	89.13	84.21	80.70
KCl	λ	130.0	122.37	119.90	115.69	111.97	107.90	102.36	98.22
	$\lambda\eta$	130.0	122.37	119.9	115.6	111.8	107.5	101.3	96.5
KBr	λ	132.2	124.31	121.78	117.69	114.14	110.32	105.30	....
	$\lambda\eta$	132.2	124.3	121.7	117.4	113.5	109.1	101.3	....
KI	λ	131.1	123.44	121.10	117.26	113.98	....	106.2	103.60
	$\lambda\eta$	131.1	123.3	120.9	116.7	112.9	....	101.4	95.3
$NaNO_3$	λ	105.2	98.07	95.57	91.35	87.16	82.21	73.99	65.81
	$\lambda\eta$	105.2	98.1	95.7	91.6	87.5	82.9	75.6	69.4
KNO_3	λ	126.3	118.10	115.12	109.78	104.71	98.67	89.18	80.41
	$\lambda\eta$	126.3	118.1	115.0	109.5	104.1	97.5	86.9	77.4
$AgNO_3$	λ	115.8	107.80	105.1	99.50	94.33	....	77.5	67.6
	$\lambda\eta$	115.8	107.80	105.1	99.50	94.33	....	79.1	71.5
HCl	λ	380.0	369.3	365.5	358.4	351.4	342	327.0	301.0
HNO_3	λ	376.5	365.0	....	353.7	346.4	....	....	....
$PbCl_2$	λ	126.3	102.1	93.2	79.2	....	....	....	....
K_2SO_4	λ	133.0	115.8	110.3	101.9	94.9	87.7	78.4	71.6
	$\lambda\eta$	133.0	116.0	110.7	102.5	96.0	89.5	82.2	78.8
Na_2SO_4	λ	111.9	95.7	....	83.64	77.07	69.95	....	....
	$\lambda\eta$	111.9	95.9	....	84.6	78.8	73.0	....	....
$ZnSO_4$	λ	115.5	72.9	63.8	52.8	45.4	39.1	....	26.2
	$\lambda\eta$	115.5	73.1	64.2	53.6	46.8	41.6	....	35.7
$CuSO_4$	λ	114.4	71.74	62.40	51.16	43.85	37.66	....	25.77
	$\lambda\eta$	114.4	72.0	62.9	52.0	45.3	40.1	....	35.3
KOH	λ	(239)	228.0	225.0	219.0	213.0	206.0	197.0	184.0

* Jour. Amer. Chem. Soc., **33**, 1436; **34**, 454, 485.

TABLE XXVIII. EQUIVALENT CONDUCTANCE (λ) AND CONDUCTANCE-VISCOSITY PRODUCT ($\lambda\eta$), AT 25° C.

$$\text{Concentration} = \frac{\text{equivalents}}{\text{liters}}.$$

Concentration		0	0.01	0.02	0.05	0.10	0.20	0.50	1.0
NaCl	λ	127.0	118.7	115.9	111.2	106.8	101.7	93.45	....
	$\lambda\eta$	127.0	118.8	116.1	111.8	107.9	103.6	97.9	....
KCl	λ	150.6	141.4	138.65	133.65	129.0	124.2	118.8	117.4
	$\lambda\eta$	150.6	141.4	138.5	133.3	128.3	123.2	117.3	115.9
KI	λ	151.3	142.3	139.4	134.7	130.8	....	....	....
	$\lambda\eta$	151.3	142.2	139.2	134.3	129.9	....	....	....
KNO_3	λ	145.4	134.9	....	126.3	120.3	....	....	....
	$\lambda\eta$	145.4	134.8	....	125.9	119.5	....	....	....
HCl	λ	426.0	411.6	406.7	398.4	390.4	380.2	....	....
	$\lambda\eta$	426.0	412.0	407.5	400.0	394.4	385.3	....	....
HNO_3	λ	420.0	406.0	....	393.3	385.0	....	....	....
	$\lambda\eta$	420.0	406.0	....	393.7	385.8	....	....	....
$PbCl_2$	λ	147.0	118.2	107.6	91.3	....	....	....	....
K_2SO_4	λ	154.8	134.4	128.1	118.15	109.9	101.4	90.4	....
	$\lambda\eta$	154.8	134.5	128.3	118.5	110.6	103.1	94.8	....
Na_2SO_4	λ	131.2	112.55	106.95	97.9	90.1	81.65	....	....
	$\lambda\eta$	131.2	112.8	107.4	98.8	91.8	85.1	....	....

TABLE XXIX. PERCENTAGE IONIZATION $\left(100\,\frac{\lambda\eta}{\lambda_0\eta_0}\right)$ AT 18° C.

Concentration = equivalents per liter

Concentration	0.01	0.02	0.05	0.10	0.20	0.50	1.0
NaCl	93.6	91.6	88.2	85.2	81.8	77.3	74.1
KCl	94.1	92.2	88.9	86.0	82.7	77.9	74.2
KBr	94.0	92.1	88.8	85.9	82.5	76.6	....
KI	94.1	92.2	89.0	86.9	....	77.3	72.7
$NaNO_3$	93.2	91.0	87.1	83.2	78.8	71.9	66.0
KNO_3	93.5	91.1	86.7	82.4	77.2	68.8	61.3
$AgNO_3$	93.1	90.8	85.9	81.4	....	68.3	61.7
HCl	97.2	96.2	94.4	92.5	....	....	....
HNO_3	97.0	....	94.0	92.1	....	....	....
$PbCl_2$	80.8	73.8	62.7	....	....	....	....
K_2SO_4	87.2	83.2	77.1	72.2	67.3	61.8	59.2
Na_2SO_4	85.7	....	75.6	70.4	65.2	....	....
$ZnSO_4$	63.3	55.6	46.4	40.5	36.0	....	30.9
$CuSO_4$	62.9	55.0	45.5	39.6	35.1	....	30.9

TABLE XXX. TRANSFERENCE NUMBERS OF THE ANION AT 18° C.

Concentration	0.01	0.02	0.05	0.1	0.2	0.5	1.0
NaCl	0.604	0.604	0.606	0.607	0.610	0.618	0.631
KCl	0.505	0.504	0.504	0.505	0.506	....	....
KBr	0.505	0.505	....	....	....	....	....
$AgNO_3$	0.529	0.529	0.529	0.529	....	....	....
HCl	0.167	0.167	0.166	0.165	0.163	0.160	0.156
HNO_3	0.160	0.159	0.156	....	....	....	....
Na_2SO_4	0.608	0.610	0.617	....	....	....	....
K_2SO_4	0.506	0.508	0.510	....	....	....	....
$Pb(NO_3)_2$	....	....	0.513	0.513	....	....	....
$MgSO_4$	0.615	0.619	0.627	....	....	....	....
$CdSO_4$	0.611	0.616	0.626	0.636	0.650	0.677	0.706
$CuSO_4$	....	0.625	0.625	0.627	0.639	0.673	....

TABLE XXXa. EQUIVALENT IONIC CONDUCTANCES (OR MOBILITIES) AT 18° C. AND 25° C.

Ion	18°	25°	Ion	18°	25°
Cs	68.0	.....	Cd	46.4	.....
Rb	67.5	.....	Mg	45.9	55.0
Tl	65.9	76.0	Cu	45.9	.....
NH_4	64.7	.....	Br	67.7	.....
K	64.5	74.8	I	66.6	76.5
Ag	54.0	63.4	Cl	65.5	75.8
Na	43.4	51.2	NO_3	61.8	70.6
Li	33.3	.....	SCN	56.7	.....
H	314.5	350	ClO_3	55.1	.....
Pb	60.8	71.0	BrO_3	47.6	54.8
Ba	55.4	65.2	F	46.7	.....
Ca	51.9	60.0	IO_3	34.0	.....
Sr	51.9	.....	SO_4	68.5	80.0
Zn	47.0	.....	C_2O_4	63.0	72.7
			OH	174	196

PROBLEMS

1. In the cell, Cd amalgam, CdI_2 solution, Cd amalgam, the observed E.M.F. at 16.3° C. is 0.0433 when c_1 and c_2 are 0.00005304 and 0.0017705 respectively. Calculate the E.M.F. of this cell.

2. In the cell, Cu amalgam (c_1), $CuSO_4$ solution, Cu amalgam (c_2), the observed E.M.F. at 20.8° C. is 0.0124 when c_1 and c_2 are 0.00016645 and 0.0004472 respectively. Calculate the E.M.F. of this cell.

3. From equations (22) and (23a) and the data in Table XXVI, calculate the ratio of zinc ions to copper ions in a system obtained by adding an excess of metallic zinc to a solution of $CuSO_4$.

4. Calculate the E.M.F. of the following cells at 25° C.:

(a) H_2 (5 atmospheres), H_2SO_4, H_2 (1 atmosphere).

(b) Cl_2 (2 atmospheres), NaCl, Cl_2 (0.1 atmosphere).

5. In the following cells, calculate the E.M.F. due to the electrode potentials, that due to the liquid junction potential and the total E.M.F. at 18° C.

(a) H_2 (1 atmosphere), HCl (0.01), HCl, (0.1), H_2 (1 atmosphere).

(b) Cl_2 (1 atmosphere), HCl, (0.01), HCl (0.1), Cl_2 (1 atmosphere).

(c) Cl_2 (1 atmosphere) NaCl (0.02), NaCl (0.20), Cl_2 (1 atmosphere).

(d) Zn, $ZnSO_4$, (0.10 *M*), $ZnSO_4$ (0.01 *M*), Zn.

(e) Hg, HgCl, KCl (1 *M*), KCl (0.1 *M*), HgCl, Hg.

(f) Hg, Hg_2SO_4, K_2SO_4 (0.005 *M*), K_2SO_4 (0.1 *M*) Hg_2SO_4, Hg.

(g) Hg, Hg_2SO_4, $ZnSO_4$ (0.01 *M*); $ZnSO_4$ (0.05 *M*) Hg_2SO_4, Hg.

6. Calculate the liquid junction potential for each of the following combinations, employing both equation (51) or (52) and equation (53). Temperature = 25° C.

(a) HCl (0.1 *M*), KCl (0.1 *M*).

(b) NaCl (0.01 *M*), KCl (0.01 *M*).

(c) KNO_3 (0.1 *M*), $NaNO_3$ (0.1 *M*).

(d) KNO_3 (0.1 *M*), $AgNO_3$ (0.1 *M*).

7. Calculate the E.M.F. of the following double concentration cells at 25° C.:

(a) K amalgam, KCl (0.01 *M*), AgCl, Ag, AgCl, KCl (0.1 *M*), K amalgam.

(b) K amalgam, KI (0.01 *M*), AgI, Ag, AgI, KI (0.1 *M*), K amalgam.

(c) Zn, $ZnSO_4$ (0.01 *M*), $PbSO_4$, Pb, $PbSO_4$, $ZnSO_4$ (0.1 *M*), Zn.

8. If the E.M.F. of the cell, H_2, (1 atmosphere), H_2SO_4 solution, O_2 (1 atmosphere) is 1.23 volts at 18° C., calculate the equilibrium constant at 18° C. for the reaction $2\,H_2 + O_2 \rightleftarrows 2\,H_2O$ (liquid). If the vapor pressure of water at 18° C. is 15.48 mm., calculate the equilibrium constant of the reaction $2\,H_2 + O_2 \rightleftarrows 2\,H_2O$ (gas). Calculate the degree of dissociation of saturated water vapor at 18° C. into hydrogen and oxygen.

9. In the lead accumulator, the following reaction occurs: $Pb + PbO_2 + 2\,H_2SO_4 = 2\,PbSO_4 + 2\,H_2O$. When the electrolyte contains 78 moles of water to 1 mole of H_2SO_4, the value of H_p is 85,700 calories and the temperature coefficient of the E.M.F. is zero. Calculate the E.M.F.

10. An accumulator containing acid of density 1.15, $(H_2SO_4 + 21\,H_2O)$, has a temperature coefficient $\frac{dE}{dT} = 4 \times 10^{-4}$, and at 17° C., its E.M.F. is 1.96 volts. Calculate the heat of the reaction.

11. Calculate the solubilities of AgBr and of AgI in water at 25° C. from the values of the E.M.F. of the following cells:

Ag, AgBr, KBr (0.1 *M*) || $AgNO_3$ (0.1 *M*), Ag; $E = 0.586$.

Ag, AgI, KI (0.1 *M*) || $AgNO_3$ (0.1 *M*), Ag; $E = 0.807$.

12. Calculate the E.M.F. of the cell: Ag, AgCl, NaCl (0.01673), NaCl (0.001674), AgCl, Ag at 18° C. if the degrees of ionization of the NaCl solutions are 92.6 and 97.3 per cent respectively.

13. The cell, Ag, AgI, KI (0.1 *M*), KBr, (0.1 *M*), AgBr, Ag has at 25° C. an E.M.F. of 0.217 volts. Determine the relative solubilities of AgBr and AgI.

14. Bodenstein and Geiger measured the E.M.F. of cells of the type H_2, HBr, Br_2 at 30° C. and obtained the following data (pressure in millimeters).

P_{HBr}	P_{Br_2}	P_{H_2}	E
12.0	0.682	742.5	0.573
2.25	1.509	753.6	0.625
1.19	1.448	760.6	0.636

Deduce therefrom the value of $\log K_p$ for the reaction $H_2 + Br_2 \rightleftarrows 2\,HBr$. Calculate the partial pressures of hydrogen and bromine above acids of the concentrations employed.

15. The dissociation pressure of Ag_2O is 5.0×10^{-4} atmosphere at 25° C. Calculate the E.M.F. of the cell: Ag, Ag_2O (solid) Ag_2O (saturated solution), O_2 (1 atmosphere).*

* (See Lewis, Z. f. physik. Chemie, **55**, 465 (1906).)

CHAPTER XVIII

SURFACE TENSION AND ADSORPTION

In this chapter we shall discuss the application of thermodynamic principles to certain properties of substances which we have hitherto neglected, viz.: to those properties which depend chiefly on the extent of surface separating different phases. We shall confine ourselves mainly to a consideration of the surfaces of liquids.

The total surface of a given mass of liquid can be increased many times by subdivision or otherwise without thereby affecting appreciably the total volume or bulk density. The increasing of the surface will be accompanied by work and heat effects, so that there will necessarily be changes in the total energy, entropy, etc., of the liquid. Since however (as we have just stated) the total volume of the liquid is essentially independent of the surface, the energy, entropy, etc., of the liquid (apart from its surface) will be unchanged when the surface is changed and we may therefore suppose that the changes in energy and entropy when the surface of a liquid is altered are changes in the energy and entropy of the surface. By the symbols, U_s, F_s, and S_s, we shall denote the total energy, the free energy and the entropy respectively of the surface.

According to equation (8) of Chap. IX, the increase in the free energy of a system is equal to the work done on it during a reversible process. Now the work done in increasing isothermally the surface of a liquid by the infinitesimal area dA will be proportional to dA, since there will be no appreciable change in the total volume and therefore $p\,dV$ will equal zero. We may therefore write

$$dF_s = \gamma\,dA, \qquad (1)$$

where γ is the work done on the liquid in increasing its surface by unit area. Similarly let q be the quantity of heat absorbed when

the surface is increased isothermally by unit area. Then we shall have for the increase in the total energy of the surface,

$$\begin{aligned} dU_s &= \gamma\, dA + q\, dA. \\ &= dF + q\, dA. \end{aligned} \tag{2}$$

If we represent by Γ the increase in the total energy due to the increase in surface by unit area, then

$$\begin{aligned} \Gamma\, dA &= \gamma\, dA + q\, dA. \\ \Gamma &= \gamma + q. \end{aligned} \tag{3}$$

Applying equation (39) of Chap. IX, Γ corresponds to $U_2 - U_1$, γ to $F_2 - F_1$; hence

$$\gamma = \Gamma + T\frac{d\gamma}{dT}, \tag{4}$$

and therefore, from equation (3),

$$q = -T\frac{d\gamma}{dT}. \tag{5}$$

Since $\frac{d\gamma}{dT}$ is negative for all liquids (except at the critical point, where it is zero), q is positive and therefore heat is always absorbed when the surface of a liquid is increased isothermally. In the case of many liquids, γ is a linear function of the temperature, i.e., $\gamma = a - bT$, so long as the temperature is not too close to the critical. Substituting in equation (4) we obtain for the total surface energy of unit area,

$$\Gamma = \gamma - T\frac{d\gamma}{dT} = a = \text{constant}. \tag{6}$$

The quantity which we have represented by γ is usually termed the surface tension; evidently it also represents the free surface energy of unit area and it is sometimes spoken of as the surface energy of unit area. The distinction between γ and Γ should however be carefully borne in mind. The surface tension γ may be expressed in ergs per square centimeter or in dynes per centimeter.

Surface Tension from the Molecular Point of View

Although the results obtained by the application of thermodynamic principles are independent of the views we may hold as to the constitution of liquids, it may be well to discuss briefly the origin of surface tension on the basis of the molecular hypothesis. From this standpoint we may imagine that there are attractive forces between molecules effective over very short distances. In the interior of a liquid the forces on a given molecule will on the average neutralize each other. The molecules in the surface layer will however be subjected to a resultant force at right angles to the surface and directed towards the interior of the liquid. When the surface of a liquid is increased by one square centimeter, a certain number of molecules which were previously in the interior have to be drawn to the surface against the molecular forces and therefore work must be done. The effect is therefore the same as if a force in the plane of the surface had to be overcome.

From this point of view we may also consider the effect of curvature of a surface on the vapor pressure of a liquid. Equilibrium between vapor and liquid is reached when the number of molecules leaving the surface per second is equal to the number returning to it. On account of the force directed inwards, only those molecules which come from the interior with a velocity greater than a certain critical value are able to pass through the surface layer and get into the vapor phase. If the surface is convex, the molecules in the surface will be pulled inwards by a smaller force than if the surface were plane. This may be easily realized by considering a molecule in the plane surface and then imagining sufficient liquid to be removed to make the surface convex. Since therefore the force on a molecule in a convex surface layer is less than on one in a plane surface layer, the critical velocity necessary to enable a molecule to penetrate the surface layer is less and therefore a larger number will leave the surface per second, thus giving rise to a greater vapor pressure. Similarly the vapor pressure at a concave surface will be less than at a plane surface. On the kinetic molecular hypothesis we can therefore show qualitatively that small drops will have a higher

vapor pressure than large ones or than a mass of liquid with a plane surface. The exact relation between vapor pressure and curvature is easily deduced thermodynamically.

Vapor Pressure of Drops

Let a spherical drop of liquid have the mass m, the radius r, vapor pressure p, surface tension γ, and density s at the temperature T. Let the vapor pressure at a plane surface of the same liquid be p_0. The density and surface tension of the larger mass of liquid will not differ appreciably from those of the small drop. We shall proceed to calculate the loss in free energy when dm grams of liquid are transferred reversibly (for example, by isothermal distillation) from the small drop to the larger mass. Assuming the vapor to be an ideal gas, the work gained in evaporating one mole of liquid from the small drop at the pressure p, expanding the vapor to the smaller pressure p_0 and finally condensing the vapor at the constant pressure p_0 is $RT \log_e \frac{p}{p_0}$. If M is the molecular weight of the vapor, we obtain for the decrease in free energy when dm grams are transferred,

$$F_1 - F_2 = dm \frac{RT}{M} \log_e \frac{p}{p_0}. \tag{7}$$

If A is the surface of the spherical drop, we have

$$m = \frac{4}{3} \pi r^3 s, \qquad dm = 4 \pi r^2 s \, dr.$$

$$A = 4 \pi r^2, \qquad dA = 8 \pi r \, dr = \frac{2}{rs} dm. \tag{7a}$$

Since dA is the decrease in the surface of the sphere when the mass dm is removed, the work to be obtained in the process is equal to $\gamma \, dA$ where γ is the surface tension and $\gamma \, dA$ is therefore the decrease in the free energy. (Adding the quantity dm to the larger mass, which may be looked on as a sphere of infinite radius, will not increase its surface appreciably). Accordingly we obtain (since $\gamma \, dA = \frac{2\gamma}{rs} dm$), from equation (7),

$$\frac{2\gamma}{rs} dm = \frac{RT}{M} \log_e \frac{p}{p_0} \cdot dm; \qquad \log_e \frac{p}{p_0} = \frac{2\gamma}{rs} \frac{M}{RT}. \tag{8}$$

Since in general p is only very slightly greater than p_0, we may write

$$p = p_0\left(1 + \frac{2\,\gamma M}{rsRT}\right). \tag{9}$$

In the case of water at 20° C.,

$$M = 18,\quad T = 291,\quad \gamma = 72.53\,\frac{\text{dynes}}{\text{cm.}},\quad s = 1,\quad R = 8.316 \times 10^7\,\frac{\text{ergs}}{\text{degree}},$$

hence

$$p = p_0\left(1 + \frac{1.08 \times 10^{-7}}{r}\right). \tag{10}$$

Accordingly a drop of water with a radius of 10^{-5} cm. will have a vapor pressure greater by one per cent than a large mass of water at 20° C. The difference in the vapor pressures of small and large drops is therefore in general exceedingly small, but it is sufficient to account for the growth of large drops at the expense of small ones. The fact that vapors can be supersaturated and that small dust particles favor the condensation of vapors can be readily accounted for if we bear in mind how the vapor pressure of a drop depends on its radius.

The results obtained by Ramsay and Aston * for the surface tension of benzene may be represented fairly accurately by the equation: $\gamma = 28.09 - 0.127\ (t - 20)$. At 20° C., we have: $\gamma = 28.09$; $\frac{d\gamma}{dT} = -0.127$, $T = 293$; $T\frac{d\gamma}{dT} = -37.21$. Applying equation (6) we obtain $\Gamma = 28.09 + 37.21 = 65.30$ ergs. In other words, the total surface energy of unit area of benzene is 65.30 ergs and this is independent of the temperature so long as the critical temperature is not approached too closely.

In studying the surface tension of liquids, it must be borne in mind that the properties of a surface layer depend on the nature of the two phases which are separated by the surface layer. In most cases however it makes very little difference whether the two phases considered are a liquid and its saturated vapor or a liquid and air.

* Zeit. f. phys. Chem. **15**, 89 (1894).

Interface Between Two Liquids

The boundary between two liquids has associated with it a certain amount of free energy just as is the case at the boundary between a liquid and a gas. The value of the free energy per cm.^{2} of interface will be the surface tension of the interface. Let A and B be two liquids partially or not at all miscible in each other. Let γ_A and γ_B be the surface tensions of pure A and pure B respectively in contact with air or their saturated vapors and let γ'_A and γ'_B be the surface tensions of A saturated with B and of B saturated with A. Also let γ_{AB} be the surface tension at the interface of the two mutually saturated liquids. Imagine the liquid B saturated with A to have a plane surface equal to two square centimeters and suppose we cover one square centimeter of it with a thin layer of liquid A saturated with B. The total free surface energy will be $\gamma'_A + \gamma'_B + \gamma_{AB}$. If the liquid A now spreads over the two square centimeters of B, the total free energy of the surfaces considered will be $2\gamma'_A + 2\gamma_{AB}$. The decrease in the free energy is $\gamma'_B - \gamma'_A - \gamma_{AB}$. According to equation (15) Chap. IX, the decrease in free energy is positive for any spontaneous process which takes place without doing any external work. Hence if $\gamma'_B - \gamma'_A - \gamma_{AB}$ is positive, liquid A will spread on liquid B. The condition that liquid A (saturated with B) shall spread on liquid B (saturated with A) may also be expressed by the inequality,

$$\gamma_{AB} < \gamma'_B - \gamma'_A. \qquad (11)$$

At 25° C. the surface tensions of pure benzene and of pure water are 28.17 and 72.05 dynes per cm. respectively. The values for benzene saturated with water and for water saturated with benzene are 27.90 and 60.19 respectively.* The surface tension at the boundary of the two layers is 34.68. Thus we have

$$\gamma'_A = 27.90, \quad \gamma'_B = 60.19 \quad \text{and} \quad \gamma_{AB} = 34.68,$$

hence

$$\gamma'_B - \gamma'_A - \gamma_{AB} = -2.39 \quad \text{or} \quad \gamma_{AB} > \gamma'_B - \gamma'_A.$$

We therefore conclude that benzene saturated with water will not spread on water saturated with benzene. If we use the values

* Harkins, Brown and Davies, Jour. Amer. Soc. **39**, 355 (1917).

for the pure liquids, then $\gamma_B - \gamma_A - \gamma_{AB} = 9.20$ and we might infer that if a drop of benzene is placed on pure water, the benzene will spread and dissolve until the surface tension of the water is reduced by the dissolved benzene.

Surface Tension of Solids

Equation (8) which shows the relation between the vapor pressure of a small drop of liquid and that of a large mass of the same liquid can evidently be applied without change to solid bodies. We can moreover deduce a relation between the solubility of small particles and the radius of the particles (assumed to be spherical) which will enable one to calculate the free energy at the surface between a solid and its saturated solution. We shall suppose that a particle of a solid of mass m and radius r is in contact with its saturated solution of concentration c_1 and osmotic pressure P_1. The letters m_2, r_2, c_2, P_2 will refer to a second particle in contact with its saturated solution. We shall suppose that the mass dm_1 of the first particle dissolves in the saturated solution under the constant osmotic pressure P_1. By means of suitable membranes (semi-permeable and otherwise) the mass dm_1 in the solution is allowed to go from the osmotic pressure P_1 to the osmotic pressure P_2. This amount of the solution is then placed in contact with the second saturated solution and the quantity dm_1 is forced out of the solution under constant osmotic pressure P_2. Assuming that the dissolved substance obeys the gas laws, the total work gained per mole is $RT \log_e \frac{P_1}{P_2}$ (if the dissolved substance is undissociated). If however the dissolved substance is ionized and i represents the actual number of molecules obtained from one dissolved molecule, the total work gained per mole will be $iRT \log_e \frac{P_1}{P_2}$, if we assume that i remains practically constant. If M is the molecular weight of the solid, then we have as the total work gained in the process we have considered,

$$W = \frac{dm_1}{M} iRT \log_e \frac{P_1}{P_2}. \qquad (12)$$

According to equations (7a) the decrease in the surface of the first particle is $dA_1 = \frac{2}{r_1 s}\, dm_1$ and the increase in the surface of the second particle is $dA_2 = \frac{2}{r_2 s}\, dm_1$. If γ is the free surface energy per cm.^{2} at the boundary of solid and solution, then the total decrease in free energy is

$$\gamma\, dA_1 - \gamma\, dA_2 = \frac{2\gamma}{s}\left(\frac{1}{r_1} - \frac{1}{r_2}\right) dm_1,$$

and this must equal W in equation (12). Thus we obtain

$$\frac{2\gamma}{s}\left(\frac{1}{r_1} - \frac{1}{r_2}\right) = i\frac{RT}{M}\log_e \frac{P_1}{P_2} = i\frac{RT}{M}\log_e \frac{c_1}{c_2}. \qquad (13)$$

If the second particle is of the ordinary size, then r_2 may be taken as infinitely great compared with r_1 and c_2 will be the solubility c_0 as ordinarily measured. Hence we obtain for the surface tension

$$\gamma = \frac{irsRT}{2M}\log_e \frac{c_1}{c_0}. \qquad (14)$$

In this formula s is the density of the solid. Equation (14) may be written analogously to equations (8) and (9),

$$\log_e \frac{c}{c_0} = \frac{2\gamma}{irs}\cdot\frac{M}{RT} \quad \text{or} \quad c = c_0\left(1 + \frac{2M}{irsRT}\right). \qquad (15)$$

Surface Tension of Solutions

The surface tension of a solution will in general differ from that of the pure solvent. From the molecular point of view, the magnitude of the surface tension depends on the work done in pulling molecules from the interior of a liquid to the surface layer. As the forces acting on the solute molecules will in general be different from those acting on the solvent molecules, we should expect differences in surface tension. Moreover on account of the differences in the molecular forces on solvent and solute molecules, the concentration of the solute molecules in the surface layer will differ from that obtaining in the bulk of the liquid. A relation between the concentrations in the surface layer and in

the bulk of the solution may be deduced by the application of thermodynamic principles.

According to the definition of the free energy function (see Chap. IX), $F = U - TS$ and $dF = dU - T\,dS - S\,dT = -S\,dT - p\,dV$, when surface effects are excluded. Applied to a dissolved substance, we have

$$dF = -S\,dT - P\,dV, \tag{16}$$

where P is the osmotic pressure of the solution. If however we include the free surface energy and if dA represents an infinitesimal increase in the surface of the liquid, then

$$dF = -S\,dT - P\,dV + \gamma\,dA. \tag{17}$$

Restricting our consideration to isothermal changes ($dT = 0$), we have

$$dF = -P\,dV + \gamma\,dA. \tag{18}$$

From equation (18) we easily obtain

$$\left(\frac{dF}{dV}\right)_A = -P; \quad \left(\frac{dF}{dA}\right)_V = \gamma; \quad \frac{\partial^2 F}{\partial V\,\partial A} = -\left(\frac{dP}{dA}\right)_V = \left(\frac{d\gamma}{dV}\right)_A. \tag{19}$$

Let N be the total number of moles of solute in the volume V and let e be the excess number at the surface per unit area. If A is the total area, then the concentration in the interior is

$$c = \frac{N - eA}{V}.$$

When N, the total number of moles, and T, the temperature, are maintained constant, all the specific properties of the solution (as represented, for example, by P, c, e, γ) are functions of the two independent variables V and A. The osmotic pressure however is determined entirely by c, the concentration in the bulk of the liquid; the same is true of e, for the surface concentration will be fixed by the internal concentration. Similarly, the surface tension will be determined solely by c or e. Thus we may write the functional equations:

$$P = f_1(c) = f_2(e) = f_3(\gamma) = f_4(V, A). \tag{20}$$

When P is constant, so also are c, e and γ. From the relation $P = f(V, A)$, we have the mathematical relation

$$\left(\frac{dA}{dV}\right)_P = -\frac{\left(\frac{dP}{dV}\right)_A}{\left(\frac{dP}{dA}\right)_V}.$$

And since $$\left(\frac{dA}{dV}\right)_P = \left(\frac{dA}{dV}\right)_c = \left(\frac{dA}{dV}\right)_e, \text{ etc.},$$

we obtain

$$\left(\frac{dA}{dV}\right)_{P,c,e} = -\frac{\left(\frac{dP}{dV}\right)_A}{\left(\frac{dP}{dA}\right)_V} = -\frac{\left(\frac{dc}{dV}\right)_A}{\left(\frac{dc}{dA}\right)_V} = -\frac{\left(\frac{de}{dV}\right)_A}{\left(\frac{de}{dA}\right)_V} = -\frac{\left(\frac{d\gamma}{dV}\right)_A}{\left(\frac{d\gamma}{dA}\right)_V}. \quad (21)$$

From the equation

$$c = \frac{N - eA}{V},$$

or

$$eA = N - cV,$$

we have $$\left(\frac{dA}{dV}\right)_c = -\frac{c}{e} = -\frac{\left(\frac{dc}{dV}\right)_A}{\left(\frac{dc}{dA}\right)_V} \text{ (from equation (21)).}$$

Now $$\left(\frac{dP}{dA}\right)_V = \frac{dP}{dc} \cdot \left(\frac{dc}{dA}\right)_V,$$

and $$\left(\frac{d\gamma}{dV}\right)_A = \frac{d\gamma}{dc} \cdot \left(\frac{dc}{dV}\right)_A.$$

And since from (19)

$$-\left(\frac{dP}{dA}\right)_V = \left(\frac{d\gamma}{dV}\right)_A,$$

we obtain $$\frac{dP}{dc} \cdot \left(\frac{dc}{dA}\right)_V = -\frac{d\gamma}{dc} \cdot \left(\frac{dc}{dV}\right)_A,$$

or $$\frac{dP}{dc} = -\frac{d\gamma}{dc} \cdot \frac{\left(\frac{dc}{dV}\right)_A}{\left(\frac{dc}{dA}\right)_V} = -\frac{c}{e}\frac{d\gamma}{dc}.$$

Thus there results finally

$$e = -c \frac{\left(\frac{d\gamma}{dc}\right)}{\left(\frac{dP}{dc}\right)}. \tag{22}$$

If we assume that the concentration in the bulk of the liquid is so small that the equation $P = cRT$ may be applied, then $\frac{dP}{dc} = RT$ and equation (22) takes the form

$$e = -\frac{c}{RT}\frac{d\gamma}{dc}. \tag{23}$$

If the solute is dissociated so that $P = icRT$, then if we assume i to be constant, $\frac{dP}{dc} = iRT$ and equation (23) becomes

$$e = -\frac{c}{iRT}\frac{d\gamma}{dc}. \tag{24}$$

Since in equation (22) $\frac{dP}{dc}$ and c are positive, e and $\frac{d\gamma}{dc}$ have opposite signs. If therefore a solute lowers the surface tension of a liquid, its concentration will be greater in the surface layer than in the bulk of the liquid, and vice versa.

Although for purposes of illustration we have considered the surface layer to be the boundary between a liquid and its vapor (or air), the results are perfectly general and apply to surfaces separating a liquid from a solid or another liquid, or a solid from a gas. The difference between the concentrations of a dissolved substance in the surface and in the bulk of a phase is spoken of as due to adsorption. Since e of equation (22) may be positive or negative, we may have either positive or negative adsorption.

According to equation (21) we have

$$\frac{\left(\frac{d\gamma}{dV}\right)_A}{\left(\frac{d\gamma}{dA}\right)_V} = \frac{c}{e}.$$

Now $\left(\frac{d\gamma}{dV}\right)_A$ has necessarily a sign opposite to that of $\frac{d\gamma}{dc}$ and therefore it has the same sign as e (equation (23)). It follows

therefore that $\left(\frac{d\gamma}{dA}\right)_v$ is always positive. Hence if the surface separating two phases (one of which is a solution) is increased while the total volume remains constant, the surface tension increases; if the surface is diminished, the surface tension diminishes. The result of this is to make the equilibrium a stable one.

Empirical Adsorption Equation

If a solution is brought in contact with a solid phase (e.g. finely divided charcoal) the solute will be positively adsorbed by the surface separating the charcoal and the solution if the surface energy is reduced by increasing the concentration of the solute. Equation (23) will apply in this case. On account of the difficulty of measuring $\frac{d\gamma}{dc}$ and e in such cases, attempts have been made to find a relation between variables which are more easily measured. If m is the mass of the adsorbent, x the mass of the solute adsorbed and if C is the equilibrium concentration in the solution, the following relation has been found to hold, viz.:

$$\frac{x}{m} = aC^{\frac{1}{n}}, \tag{25}$$

where a and n ($n > 1$) are constants for a given solution and adsorbent. It is assumed that the total surface active is proportional to the mass of the adsorbent and this means that the adsorbent must be used in the same state of subdivision in different experiments. Equation (25) is the analytical expression for the general parabola and is not an "exponential" equation, as we sometimes find it stated. The equation may also be written

$$\log\left(\frac{x}{m}\right) = \frac{1}{n}\log C + \log a, \tag{26}$$

so that if we plot $\log\frac{x}{m}$ as ordinates against $\log C$ as abscissæ we should obtain a straight line. The value of a or $\log a$ depends to a great extent on the units employed in expressing x, m and C. The value of $\frac{1}{n}$ is more characteristic. The following values of $\frac{1}{n}$

as determined by Freundlich * refer to blood charcoal as the adsorbent and (unless otherwise stated) to water as the solvent.

TABLE XXXI. ADSORPTION BY BLOOD CHARCOAL

Solute	$\frac{1}{n}$	Solute	$\frac{1}{n}$
Formic acid	0.451	Benzoic acid	0.338
Acetic acid	0.425	Chlorine	0.297
Propionic acid	0.394	Bromine	0.340
Butyric acid	0.301	Picric acid (in alcohol)	0.230
Monochloracetic acid	0.363	Benzoic acid (in benzene)	0.416
Succinic acid	0.243	Bromine (in ether)	0.263

Electrocapillary Adsorption

In case the solute in a solution is dissociated into ions, and the solution is in contact with a liquid or solid phase, it may happen that the ions are adsorbed at the bounding surface, forming a Helmholtz "double layer." Let us assume that such is the case. This double layer will have the properties of a condenser with a certain potential difference and a certain charge per square centimeter of surface. If dQ is the electric charge (due to the adsorbed ions) on the element of surface dA and if the surface is increased at constant temperature and volume by dA, the work necessary is $\gamma\, dA + E\, dQ$ and the heat absorbed is $T\, dS$ where S is the entropy. Hence we have for the increase in energy $dU = T\, dS + \gamma\, dA + E\, dQ$. This may be written $d(U - TS - EQ) = -S\, dT + \gamma\, dA - Q\, dE$, or since the temperature is maintained constant,

$$d(U - TS - EQ) = \gamma\, dA - Q\, dE. \qquad (27)$$

Since $d(U - TS - EQ)$ is a perfect differential,

$$\frac{\partial^2 (U - TS - EQ)}{\partial A\, \partial E} = \left(\frac{d\gamma}{dE}\right)_A = -\left(\frac{dQ}{dA}\right)_E. \qquad (28)$$

* Kapillarchemie, p. 150.

If e' is the number of equivalents of adsorbed ions per square centimeter, then $\left(\frac{dQ}{dA}\right)_E = e'F_v$ where F_v is a faraday. Hence from (28)

$$e' = -\frac{1}{F_v}\left(\frac{d\gamma}{dE}\right)_A. \tag{29}$$

When Q is expressed in coulombs and E in volts, $Q\,dE$ of equation (27) is expressed in joules. We must multiply $Q\,dE$ by 10^7 to reduce it to ergs, the units in which $\gamma\,dA$ is expressed when γ is given in dynes per cm. and dA in cm.^{2} We thus obtain for the electrocapillary adsorption in equivalents per cm.^{2},

$$e' = -\frac{1}{10^7 F_v}\left(\frac{d\gamma}{dE}\right)_A. \tag{29a}$$

Finally if N_s is the number of equivalents of the salt in 1 gram-molecular weight, then the number of moles e'' of salt adsorbed (as ions) per square centimeter is

$$e'' = -\frac{1}{10^7 N_s F_v}\left(\frac{d\gamma}{dE}\right)_A. \tag{30}$$

CHAPTER XIX

RADIATION, QUANTUM THEORY, NERNST HEAT THEOREM

If two bodies at different temperatures are put in contact, the temperatures of the two bodies will in time become equal. We have described this process (see Chap. III) by saying that heat has passed from the hotter to the colder body. This transfer of energy by contact of two bodies at different temperatures is sometimes referred to as the conduction of heat. But even if the two bodies are not in contact and are separated by a vacuum, transfer of energy will take place through the vacuum and in this case we speak of the transfer of energy by radiation. Radiation from one body to another can also occur even if the bodies are separated by a material medium. Experiment has shown that this radiation follows all the laws which govern visible radiation. Thus we can apply to all forms of radiation, whether visible or not, the laws governing the reflection, refraction and propagation of light rays. In our brief treatment of the subject we shall restrict ourselves to radiation that is unpolarized and of uniform intensity in all directions and we shall suppose that the medium of propagation is a vacuum or what is practically equivalent to this, air at atmospheric pressure. For a complete and rigorous treatment the student should consult Planck's Theory of Heat Radiation.

Let $d\sigma$ represent an infinitely small element of area in the interior of a medium through which radiation is passing. Any direction through $d\sigma$ may be specified by the angles θ and ϕ, where θ is the angle the given direction makes with the normal to $d\sigma$ and where the azimuth ϕ is the angle which the projection of the direction on the surface $d\sigma$ makes with a given line in the plane of $d\sigma$. The energy radiated through $d\sigma$ in a given direction in the time dt is evidently proportional to $d\sigma$, to the time dt and

to the cosine of the angle θ. Thus if $\theta = \frac{\pi}{2}$, the radiation through $d\sigma$ in the direction θ will vanish. A finite amount of energy is however not present along a mathematical line. We may look on every point of the element $d\sigma$ as the vertex from which radiation passes in all directions. And instead of a mathematical line defined by θ and ϕ, we shall consider the radiation in the infinitely small cone limited by $\theta + d\theta$ and $\phi + d\phi$. The solid angle of this cone (the area cut out of the surface of a sphere of unit radius with center in $d\sigma$ by our infinitely small cone) is

$$d\Omega = \sin\theta \cdot d\theta\, d\phi.$$

Accordingly the energy radiated in the time dt through $d\sigma$ in the direction of the cone $d\Omega$ is proportional to dt, to $d\sigma$, to $\cos\theta$ and to the solid angle $d\Omega$. If K is the proportionality factor, we have for the energy radiated in time dt

$$K\, dt\, d\sigma \cos\theta\, d\Omega = K\, dt\, d\sigma \sin\theta \cos\theta\, d\theta\, d\phi. \qquad (1)$$

The quantity K we shall call the intensity of radiation in the direction (θ, ϕ). For the total radiation through $d\sigma$ toward one side, we have

$$\int_0^{2\pi} d\phi \int_0^{\pi} d\theta \cdot K \sin\theta \cos\theta\, d\sigma\, dt.$$

Since we assume that the radiation is uniform in all directions, K is a constant and we finally obtain on integration

$$\pi K\, d\sigma\, dt. \qquad (2)$$

If we let R be the energy radiated in one second by a square centimeter towards one side, we have

$$R = \pi K. \qquad (3)$$

Space Density of Radiation

Since energy is radiated in air or a vacuum with the finite velocity $c = 3 \times 10^{10}\ \frac{\text{cm.}}{\text{sec.}}$, there must be in every cubic centimeter of space the finite amount of energy of radiation, u. Consider a small volume v and with any point O in this volume as center construct a sphere with the radius r. Let $d\sigma$ be any ele-

ment of surface of the sphere. From any point in $d\sigma$ as vertex consider a cone passing through v and cutting out a volume with cross-section f and length s. The radiation from $d\sigma$ in this small cone will take $\frac{s}{c}$ seconds in traversing the length s. The solid angle of the cone is $\frac{f}{r^2}$; $\theta = 0$ since the direction of the cone is perpendicular to $d\sigma$. The energy in the volume fs is, according to equation (1),

$$K \frac{s}{c} d\sigma \frac{f}{r^2} = K\, d\sigma \cdot \frac{fs}{r^2 c}.$$

This energy enters v and spreads out into the volume fs. Summing up over all conical elements which have their vertex in $d\sigma$ and enter v, we obtain

$$K \frac{d\sigma}{r^2 c} v.$$

This is the total energy in v due to the radiation from the element $d\sigma$. Assuming K to be uniform in all directions, we have for the total energy passing through the total surface of the sphere and entering the volume v, since the total area is $4\pi r^2$,

$$4\pi \frac{Kv}{c}.$$

Hence we obtain for the energy density u,

$$u = \frac{4\pi K}{c}, \tag{4}$$

and from equation (3)

$$u = 4 \frac{R}{c}. \tag{5}$$

The Stefan-Boltzmann Law

We shall define a "black" body as one which absorbs completely all radiation incident on it. The radiation in equilibrium with a black body is a function of the temperature of the black body and we shall speak of the radiation as having the same temperature as the black body. On the electromagnetic theory of radiation, radiation incident on a completely reflecting surface or on a black body exerts a pressure which is equal to one-third

the space density of the energy of the radiation. Thus if u is the energy of the radiation per cubic centimeter, we have

$$p = \frac{u}{3}. \tag{6}$$

This deduction from electromagnetic theory has been confirmed experimentally. Let us imagine a cylinder containing a black body at the temperature T and enclosed by a movable piston on which the radiation exerts a pressure p. The whole apparatus may be supposed for simplicity's sake to be in a vacuum. Let U, V, and S be the total energy, total volume and total entropy of the radiation in the cavity. We shall have $U = Vu$. Let us imagine that the system undergoes an infinitesimal reversible change of state, accompanied by changes in U, S and V. These changes will be determined by the equation

$$dS = \frac{dU + p\,dV}{T}. \tag{7}$$

We shall express all variations in terms of the two independent variables T and V. Hence since u is a function of T alone, we have $dU = V\frac{du}{dT}\,dT + u\,dV$. Substituting in (7), and bearing equation (6) in mind, we obtain

$$dS = \frac{V}{T}\frac{du}{dT}\,dT + \frac{4}{3}\frac{u\,dV}{T}. \tag{8}$$

From (8) we obtain the partial derivatives:

$$\left(\frac{dS}{dT}\right)_V = \frac{V}{T}\frac{du}{dT}; \qquad \left(\frac{dS}{dV}\right)_T = \frac{4}{3}\frac{u}{T}. \tag{9}$$

Differentiating the expressions in (9) partially with respect to V and T, we have

$$\frac{\partial^2 S}{\partial T\,\partial V} = \frac{1}{T}\frac{du}{dT} = \frac{4}{3T}\frac{du}{dT} - \frac{4}{3}\frac{u}{T^2}.$$

This gives us

$$\frac{du}{dT} = \frac{4u}{T} \quad \text{and finally,} \quad u = aT^4. \tag{10}$$

where a is a constant of integration. Equation (10) is an expression of the Stefan-Boltzmann Law. Employing equation (5) we may express (10) in the following form:

$$R = \frac{ac}{4} T^4 = \sigma T^4. \tag{11}$$

Wien's Displacement Laws

The total intensity K of unpolarized black body radiation may be looked on as a sum of contributions from the various parts of the complete spectrum. Thus if we consider that part of the spectrum contained within the limits λ and $\lambda + d\lambda$ the contribution from this region will be proportional to $d\lambda$ and may be represented by $E_\lambda\, d\lambda$. Accordingly we have for the sum of all contributions

$$K = \int_0^\infty E_\lambda\, d\lambda. \tag{12}$$

We shall call E_λ the intensity of radiation of wave-lengths lying in the spectral region λ to $\lambda + d\lambda$ or more simply the intensity of radiation of wave-length λ. It should be noted however that E_λ and K are of different dimensions. The general problem of the distribution of energy in the spectrum consists in determining E_λ as a function of λ and the temperature.

Since in equation (12) K is always finite, E_λ must equal zero, not only when $\lambda = 0$ but also when $\lambda = \infty$. A curve expressing E_λ as a function of λ must therefore exhibit at least one maximum point. A complete solution of the problem is not possible on the basis of thermodynamics alone and a satisfactory solution is not obtainable even on the basis of the classical electromagnetic theory and the classical dynamics. Wien was however able to deduce two important results without its being necessary to find the exact form of the functional relation between E_λ, λ and T. If λ_m represents the wave-length corresponding to the maximum value of E_λ (which we shall call $E_{\max.}$), then Wien found the two following relationships: —

$$\left.\begin{aligned} \lambda_m T &= b = \text{const.} \\ E_{\max.} &= kT^5. \end{aligned}\right\} \tag{13}$$

The wave-length λ_m corresponding to the maximum value of E is inversely proportional to the absolute temperature and therefore shifts towards the shorter wave-lengths as the temperature is increased. The second equation of Wien's indicates that the value of the maximum intensity in the spectrum is proportional to the fifth power of the absolute temperature.

Planck's Distribution Formula

In deducing his distribution formula for radiation in equilibrium with vibrating systems of atoms or electrons, Planck made the following important assumptions:

(1) The vibrators or oscillators are able to absorb energy of radiation in a perfectly continuous manner.

(2) When an atom or electron or other oscillator emits radiation, it can do so only in multiples of a certain unit $\epsilon = h\nu$ where h is a universal constant and ν is the frequency of the radiation emitted.

(3) When an oscillator by absorption has acquired energy equal to a multiple of the unit ϵ, it may or may not emit it, but if emission takes place, the total quantity of absorbed energy is emitted.

(4) The ratio of the probability that no emission takes place to the probability that emission does take place is proportional to the intensity of the vibration which excites the oscillator.

It will be observed that the quantum of energy $\epsilon = h\nu$ is not a fixed quantity, but is proportional to the frequency of the radiation considered. If we let $u_\lambda\, d\lambda$ be the energy per cubic centimeter due to radiation between the wave-lengths λ and $\lambda + d\lambda$, then evidently

$$u = \int_0^\infty u_\lambda\, d\lambda.$$

Also from equations (4) and (12) we have

$$u = \frac{4\pi}{c} K = \frac{4\pi}{c} \int_0^\infty E_\lambda\, d\lambda.$$

Hence

$$u_\lambda = \frac{4\pi}{c} E_\lambda. \tag{14}$$

Now Planck obtained for E_λ or u_λ referred to monochromatic unpolarized light of wave-length λ the expressions:

$$E_\lambda = \frac{2\,c^2h}{\lambda^5} \cdot \frac{1}{e^{\frac{ch}{k\lambda T}} - 1}. \tag{15}$$

$$u_\lambda = \frac{8\,\pi ch}{\lambda^5}\left(\frac{1}{e^{\frac{ch}{k\lambda T}} - 1}\right). \tag{16}$$

In these expressions, k is the gas-constant per molecule; that is, if the equation $pV = RT$ refers to one mole of an ideal gas and if N is the number of molecules (6.062×10^{23}) in one mole, then

$$k = \frac{R}{N}.$$

Equation (16) may be expanded into the following:

$$u_\lambda = \frac{8\,\pi ch}{\lambda^5}\left[e^{-\frac{ch}{k\lambda T}} + e^{-\frac{2ch}{k\lambda T}} + e^{-\frac{3ch}{k\lambda T}} + \cdots\right]. \tag{17}$$

We obtain therefore on integration by parts

$$u = \int_0^\infty u_\lambda\, d\lambda = 48\,\pi ch\alpha\left(\frac{kT}{ch}\right)^4,$$

where $$\alpha = 1 + \frac{1}{2^4} + \frac{1}{3^4} + \cdots = \frac{\pi^4}{90} = 1.0823.$$

This may be written as follows:

$$u = \frac{48\,\pi k^4\alpha}{c^3h^3} \cdot T^4 = aT^4, \tag{18}$$

which gives the proportionality factor a of the Stefan-Boltzmann law in terms of k and h. Thus

$$a = \frac{48\,\pi k^4\alpha}{c^3h^3}. \tag{19}$$

From equation (15) we find the condition that E_λ shall be a maximum by putting $\frac{dE_\lambda}{d\lambda}$ equal to zero. Putting $x = \frac{ch}{\lambda_m kT}$, we obtain as the condition

$$e^{-x} + \frac{x}{5} - 1 = 0, \tag{20}$$

the solution of which is $x = 4.9651$. Hence

$$\lambda_m T = \frac{ch}{xk} = b \text{ (of equation (11))}. \tag{21}$$

The value of $\frac{ch}{k}$ in equation (15) has been determined by a number of investigators to be equal to 1.436 cm. degree. Hence we calculate b of equation (21) to be equal to $\frac{1.436}{4.9651} = 0.289$ whereas Lummer and Pringsheim found 0.294 and Paschen found 0.292. The most recent value of a of the Stefan-Boltzmann equation is 7.39×10^{-15} obtained by Westphal. Employing

$$\frac{ch}{k} = 1.436,$$

and

$$a = 7.39 \times 10^{-15} = \frac{48\,\pi k^4 \alpha}{c^3 h^3},$$

we obtain $k = 1.34 \times 10^{-16}$ and $h = 6.415 \times 10^{-27}$. A very accurate value for k can be obtained in an independent manner. Since

$$k = \frac{R}{N},$$

where R is the gas-constant for one mole of an ideal gas and N is Avogadro's number, we have

$$k = \frac{8.316 \times 10^7}{6.062 \times 10^{23}} = 1.37 \times 10^{-16} \frac{\text{ergs}}{\text{degree}}. \tag{22}$$

A presumably accurate value of h may be obtained in the following way. The Rydberg constant for the Balmer series in the hydrogen spectrum is 3.290×10^{15} and this according to Bohr's* theory of the atom is equal to $\frac{2\,\pi e^4 m}{h^3}$. Now the value of e, the charge on an electron, is equal to 4.774×10^{-10} electrostatic units and the ratio $\frac{e}{m} = 1.767 \times 10^7$, from which data the value of h is

$$h = 6.547 \times 10^{-27}. \tag{23}$$

* Phil. Mag. **26,** 476, 857 (1913); **27,** 506 (1914); **30,** 394 (1915).

From (22) and (23) we obtain as an accurate value of the ratio $\frac{h}{k}$ which we shall represent by β,

$$\beta = \frac{h}{k} = 4.779 \times 10^{-11}. \tag{24}$$

Energy of Vibrating Atoms

Planck obtains for the energy of vibration of a system of linear oscillators an expression which, applied to a system of atoms in a solid body, becomes

$$U = 3\,Nh\nu \left(\frac{1}{e^{\frac{h\nu}{kT}} - 1} + \frac{1}{2} \right), \tag{25}$$

where N is the number of atoms. If N represents Avogadro's number, $Nh\nu$ is equal to $Nk \cdot \frac{h}{k}\nu = R\beta\nu$ and equation (25) becomes

$$U = 3RT \left[\frac{\frac{\beta\nu}{T}}{e^{\frac{\beta\nu}{T}} - 1} + \frac{\beta\nu}{2\,T} \right]. \tag{26}$$

According to (26) when $T = 0$, U does not become zero but equal to $\frac{3}{2} R\beta\nu$ whereas when T is very large $U = 3\,RT$. By differentiating with respect to T, we obtain for the atomic heat of a solid at constant volume

$$C_v = \frac{dU}{dT} = 3\,R \cdot \frac{\left(\frac{\beta\nu}{T}\right)^2 e^{\frac{\beta\nu}{T}}}{\left(e^{\frac{\beta\nu}{T}} - 1\right)^2}. \tag{27}$$

This expression, first applied by Einstein to solid bodies, will be called Einstein's specific heat formula. It will be observed that when $T = 0$, $C_v = 0$, and when T is large, C_v approaches the value $3\,R = 5.96$ (Law of Dulong and Petit). Einstein's formula reproduces the atomic heat of the diamond with considerable accuracy, but in many other cases it has been found to be inadequate. Nernst and Lindemann proposed an empirical

formula which was found to give a very accurate reproduction of the experimental data. Their formula for atomic heat is

$$C_v = \frac{3}{2} R \left[\frac{\left(\frac{\beta\nu}{T}\right)^2 \cdot e^{\frac{\beta\nu}{T}}}{\left(e^{\frac{\beta\nu}{T}} - 1\right)^2} + \frac{\left(\frac{\beta\nu}{2T}\right)^2 \cdot e^{\frac{\beta\nu}{2T}}}{\left(e^{\frac{\beta\nu}{2T}} - 1\right)^2} \right]. \tag{28}$$

Since experiment always gives C_p, Nernst and Lindemann proposed the following formula which is very useful in calculating C_v from C_p, viz.:

$$C_p = C_v + aT^{\frac{3}{2}}, \tag{29}$$

where a is a constant characteristic of each substance.

Debye's Formula for Atomic Heat

A very considerable advance in the theory of the specific heat of solids was made by Debye * who, instead of supposing that all the atoms in a solid vibrate with a single characteristic frequency ν, maintained that the vibrations must be very complex and that if a body consists of N atoms, the system will in general exercise $3N$ different periodic vibrations. According to Debye there is a definite limiting frequency ν_m beyond which the spectrum does not extend. Debye obtains for the energy of a solid containing N atoms

$$U - U_0 = \frac{9N}{\nu_m^3} \int_0^{\nu_m} \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1} \cdot \nu^2 \, d\nu, \tag{30}$$

where U_0 is the energy at the absolute zero.

If we introduce the temperature $\theta = \beta\nu_m$, characteristic of each substance and substitute the letter y for $\frac{\beta\nu}{T}$, we obtain, since $Nk = R$,

$$U - U_0 = 9RT \left(\frac{T}{\theta}\right)^3 \int_0^{\frac{\theta}{T}} \frac{y^3 \, dy}{e^y - 1}. \tag{31}$$

Writing x for the fraction $\frac{\theta}{T} = \frac{\beta\nu_m}{T}$ and differentiating with respect to T, we obtain, since $C_v = \frac{dU}{dT}$,

$$\frac{C_v}{3R} = \frac{12}{x^3} \int_0^x \frac{y^3 \, dy}{e^y - 1} - \frac{3x}{e^x - 1}. \tag{32}$$

* Ann. der Physik [4], **39**, 789 (1912).

From (31) and (32) we obtain

$$U - U_0 = \frac{9\,RT}{12}\left[\frac{C_v}{C_\infty} + \frac{3\,x}{e^x - 1}\right]; \quad x = \frac{\beta\nu_m}{T}; \quad C_\infty = 3\,R. \quad (32a)$$

Atomic Heat at Moderate and at High Temperatures

The expressions $\frac{y^3}{e^y - 1}$ and $\frac{3\,x}{e^x - 1}$ can be expanded in an infinite series. Thus (see page 106, Edwards' Differential Calculus, Third Edition),

$$\frac{x}{e^x - 1} = 1 - \frac{x}{2} + \sum_{n=1}^{n=\infty} (-1)^{n-1} \cdot \frac{B_n}{(2\,n)!} \cdot x^{2n},$$

where B_n is the nth Bernoullian number. For example,

$$B_1 = \frac{1}{6},\ B_2 = \frac{1}{30},\ B_3 = \frac{1}{42},\ B_4 = \frac{1}{30},\ B_5 = \frac{5}{66},\ B_6 = \frac{691}{2730},\ B_7 = \frac{7}{6}.$$

Expanding both $\frac{y^3}{e^y - 1}$ and $\frac{3\,x}{e^x - 1}$, and carrying out the integration in equation (32), we obtain

$$\frac{C_v}{3\,R} = 1 - 3\sum_{n=1}^{n=\infty} (-1)^{n-1} \frac{2\,n - 1}{2\,n + 3} \cdot \frac{B_n}{(2\,n)!} \cdot x^{2n}$$

$$= 1 - \frac{x^2}{20} + \frac{x^4}{560} - \frac{x^6}{18{,}144} + \frac{x^8}{633{,}600} - \frac{x^{10}}{23{,}063{,}040} + \cdots \quad (33)$$

This series may be used to calculate C_v when x is less than 2, i.e., when $T > \frac{\beta\nu_m}{2}$.

Atomic Heat at all Temperatures

The expression $\frac{y^3}{e^y - 1}$ may also be expanded as follows:

$$\frac{y^3}{e^y - 1} = y^3\,(e^{-y} + e^{-2y} + e^{-3y} + \cdots) = \sum_{n=1}^{n=\infty} y^3 e^{-ny}.$$

Now we have

$$\int_0^x y^3 e^{-ny}\,dy = \int_0^\infty y^3 e^{-ny}\,dy - \int_x^\infty y^3 e^{-ny}\,dy$$
$$= \frac{6}{n^4} - x^4 e^{-nx}\left(\frac{1}{nx} + \frac{3}{n^2x^2} + \frac{6}{n^3x^3} + \frac{6}{n^4x^4}\right).$$

Therefore we obtain

$$\int_0^x \frac{y^3}{e^y - 1}\,dy = \int_0^x \sum_{n=1}^{n=\infty} y^3 e^{-ny}\,dy$$
$$= \sum_{n=1}^{n=\infty} \frac{6}{n^4} - x^4 \sum_{n=1}^{n=\infty} e^{-nx}\left[\frac{1}{nx} + \frac{3}{n^2x^2} + \frac{6}{n^3x^3} + \frac{6}{n^4x^4}\right].$$

Now the value of $\sum_{n=1}^{n=\infty} \frac{1}{n^4}$ is $\frac{\pi^4}{90} = 1.0823$. Accordingly from (32), we obtain

$$\frac{C_v}{3R} = \frac{4\pi^4}{5}\cdot\frac{1}{x^3} - \frac{3x}{e^x - 1} - 12x\sum_{n=1}^{n=\infty} e^{-nx}\left(\frac{1}{nx} + \frac{3}{n^2x^2} + \frac{6}{n^3x^3} + \frac{6}{n^4x^4}\right). \tag{34}$$

At very low temperatures and therefore for large values of x, we have

$$\frac{C_v}{3R} = \frac{4\pi^4}{5}\left(\frac{T}{\theta}\right)^3 = 77.927\,\frac{T^3}{(\beta\nu_m)^3}. \tag{35}$$

Debye's formula, therefore, leads to the result that at very low temperatures the atomic heat is proportional to the third power of the absolute temperature. Debye's formula has been found to hold with considerable accuracy and on account of its theoretical basis is to be preferred to that of Nernst and Lindemann. In most cases the value of ν_m agrees closely with the characteristic frequency ν of the Einstein and Nernst and Lindemann equations.

As an illustration of the applicability of the formulas of Debye and of Nernst and Lindemann, we give in Table XXXII the values of C_p for silver, as calculated by both equations.

TABLE XXXII. SILVER, $\beta\nu = 215$

T	C_p observed	C_p Debye	C_p Nernst and Lindemann
35.0	1.58	1.50	1.59
39.1	1.90	1.88	1.92
42.9	2.26	2.14	2.22
45.5	2.47	2.42	2.44
51.4	2.81	2.85	2.82
53.8	2.90	3.02	2.98
77.0	4.07	4.19	4.11
100.0	4.86	4.83	4.77
200.0	5.78	5.80	5.77
273.0	6.00	6.04	6.02
331.0	6.01	6.13	6.12
535.0	6.46	6.46	6.45
589.0	6.64	6.57	6.57

Determination of Characteristic Frequencies

A number of methods are in use for determining the frequency characteristic of a given solid. We shall describe them very briefly.

First Method

When radiation from a black body falls on the surface of a given solid, part of the radiation is reflected, part is transmitted and part is absorbed. Certain wave-lengths will be more completely absorbed than others, so that we shall have one or more absorption maxima. Now the radiation which is most strongly absorbed is also that which is most completely reflected, at least when the absorption maxima lie in the infra-red region of the spectrum. If therefore radiation of all wave-lengths be successively reflected from a number of pieces of a solid, the reflected radiation will, after each reflection, approximate more and more closely to that which is most strongly absorbed, and which we may consider as corresponding to the characteristic frequency of the solid. This method has been developed principally by Rubens and his co-workers. We may call it the method of Residual Rays. The following table contains some of the results as given by Rubens and Wartenberg.*

* Sitzungber. königl. preuss. Akad., p. 169 (1914).

TABLE XXXIII. RESIDUAL RAYS

Substance	Wave-length in μ	Substance	Wave-length in μ
NH_4Cl	51.5	$PbCl_2$	91.0
$NaCl$	52.0	KI	94.1
NH_4Br	59.3	$HgCl_2$	95.0 approx.
KCl	63.4	$CaCO_3$	98.7
$AgCl$	81.5	$HgCl$	98.8
KBr	82.6	$AgBr$	112.7

Second Method

From a consideration of the forces acting on atoms when displaced from their positions of equilibrium, Einstein* deduced the following approximate formula for the characteristic frequency ν, viz.:

$$\nu = 2.54 \times 10^{7} \frac{V^{\frac{1}{3}}}{M^{\frac{1}{2}} K^{\frac{1}{2}}},$$

where K is the compressibility, V the atomic (or molecular) volume, and M the atomic (or molecular) weight.

Third Method

On the assumption that at the melting-point, T_s, of a solid, the amplitude of vibration of the atoms is equal to the mean distance of the atoms apart, F. A. Lindemann,† derived the formula

$$\nu = 2.80 \times 10^{12} \sqrt{\frac{T_s}{M V^{\frac{2}{3}}}}.$$

Lindemann also proposed another method based on a relation between the characteristic frequency in the infra-red and the characteristic frequency in the ultra-violet. The characteristic frequency or (what is equivalent to this) the value of $\beta\nu$ is sometimes determined by finding what value of it will make the Nernst and Lindemann formula for specific heat fit the experimental results. We may finally mention that Debye in connection with his specific heat formula has deduced a rather complicated relation between the maximum frequency ν_m and

* Ann. der Physik [4], **34**, 170 (1911). † Physik. Zeit. 11, 609 (1910).

the density, compressibility, and other elastic constants of the solid.

Most of the methods just suggested apply in strictness to monatomic solids only. If applied to a substance like AgI or $PbCl_2$, the value of $\beta\nu$ obtained can only represent a sort of average value. The attempt has been made with some success to represent the molecular heat of a compound as the sum of terms corresponding to the Nernst and Lindemann formula (equation (28)). Thus if we represent equation (28) by the symbol $f(\beta\nu)$, then the molecular heat of $PbCl_2$ may be represented according to Pollitzer * by the expression $f(85) + 2f(270)$. A different method has been suggested by Nernst in the case of salts of the type KCl, KBr or NaCl. If ν_1 represents the frequency obtained by applying the melting-point formula of Lindemann and if ν_2 is the frequency obtained by the method of Residual Rays, then the molecular heat is equal to

$$F_1\left(\frac{\beta\nu_1}{T}\right) + F_2\left(\frac{\beta\nu_2}{T}\right),$$

where F_1 and F_2 are the Debye and Einstein expressions respectively for the atomic heat.

Affinity of Processes

The determination of the affinity of a reaction is recognized to be of great theoretical and practical importance and we have in preceding chapters deduced relations connecting the affinity of a process with the heat of the reaction. The fundamental formula (see equation (37), Chap. IX) for a reaction carried out reversibly at constant pressure and temperature is

$$A = H_p + T\left(\frac{dA}{dT}\right)_p. \tag{36}$$

This may be written in the following forms:

$$\left(\frac{d\left(\frac{A}{T}\right)}{dT}\right)_p = -\frac{H_p}{T^2}. \tag{37}$$

* Zeit. für Elekt. **19**, 513 (1913).

$$A = T\int^{T} -\frac{H_p}{T^2}dT. \tag{38}$$

$$A = H_p - T\int^{T} \frac{1}{T}\frac{dH_p}{dT}\,dT. \tag{39}$$

$$A = H_p - T\int^{T} \frac{(C_1 - C_2)_p}{T}\,dT. \tag{40}$$

From purely thermal or thermochemical measurements (which give us a knowledge of C_1, C_2, H_p, etc.), it is evident that it is impossible to determine the value of A since the indefinite integrals in equations (38), (39) and (40) contain an arbitrary constant of integration which cannot be determined by the first and second laws of thermodynamics. In order to calculate A we need to know in addition to H_p, the value of $\left(\frac{dA}{dT}\right)_p$ (which means a knowledge of A at a series of temperatures) and then we immediately find A from equation (36), or we must know the value of A at some one temperature when we can find A at any other temperature by means of the following relation deducible from equation (38):

$$\frac{A_2}{T_2} - \frac{A_1}{T_1} = \int_{T_1}^{T_2} -\frac{H_p}{T^2}\,dT. \tag{41}$$

Thus if H_p is known as a function of the temperature and if A_1 at the temperature T_1 is known, then A_2 at the temperature T_2 is fixed unambiguously. A very important advance in the treatment of this problem was made by Nernst, but before proceeding to a consideration of his heat theorem, we shall see what information we can obtain without the assumptions made by Nernst. Restricting our considerations to processes occurring in condensed systems (solids or pure liquids), we shall assume merely that $\left(\frac{dA}{dT}\right)_p$ is finite. For the time being we shall drop the subscript p from H_p. According to equation (36) if $\left(\frac{dA}{dT}\right)_p$ is always finite, $A = H$ at the absolute zero, or $A_0 = H_0$. From equation (36) we have also

$$\left(\frac{dA}{dT}\right)_p = \frac{A - H}{T}. \tag{42}$$

At the absolute zero, $\left(\frac{dA}{dT}\right)_p = \frac{0}{0}$. According to a well-known theorem of the differential calculus, we must have, when $T = 0$

$$\frac{dA}{dT} = \frac{\frac{dA}{dT} - \frac{dH}{dT}}{1}. \tag{43}$$

And since $\frac{dA}{dT}$ is supposed to be finite, we conclude that at the absolute zero,

$$\frac{dH}{dT} = 0 = C_1 - C_2. \tag{44}$$

This result is in harmony with the various formulas for the heat capacities of solids which would make not only $C_1 - C_2$ equal to zero but $C_1 = 0$ and $C_2 = 0$ when $T = 0$. From equation (36) we obtain on differentiating,

$$\frac{dA}{dT} = \frac{dH}{dT} + \frac{dA}{dT} + T\frac{d^2A}{dT^2},$$

and hence

$$\frac{d^2A}{dT^2} = -\frac{1}{T}\frac{dH}{dT} = -\frac{C_1 - C_2}{T}.$$

According to either the Nernst and Lindemann or the Debye formulas for heat capacity, $\frac{C_1}{T}$ is zero when $T = 0$. For example, according to equation (35) the heat capacity of a solid is proportional to T^3 at low temperatures and hence $\frac{C}{T}$ becomes zero when $T = 0$. We therefore conclude that $\frac{d^2A}{dT^2} = 0$ when $T = 0$. Similarly we could show that $\frac{d^2H}{dT^2} = 0$ at the absolute zero. These results have been obtained, assuming $\frac{dA}{dT}$ to be finite and employing either the Nernst and Lindemann or the Debye formula for the heat capacity of a solid. The next step would be to show that $\left(\frac{dA}{dT}\right)_p$ is not only finite but equal to zero and this is the assumption at the basis of the Nernst Heat Theorem.

Nernst Heat Theorem

Nernst assumes that for any process in a condensed system at the absolute zero,

$$\left(\frac{dA}{dT}\right)_v = 0 \text{ when } T = 0. \tag{45}$$

Comparing equations (36) and (39), we see that

$$\left(\frac{dA}{dT}\right)_v = -\int^T \frac{1}{T}\frac{dH}{dT}dT. \tag{46}$$

Employing Nernst's assumption, as given in (45) we have

$$\lim_{T=0}\left(\frac{dA}{dT}\right)_v = -\int^0 \frac{1}{T}\frac{dH}{dT}dT = 0. \tag{47}$$

Subtracting equation (47) from (46) we obtain

$$\left(\frac{dA}{dT}\right)_v = -\int_0^T \frac{1}{T}\frac{dH}{dT}dT, \tag{48}$$

and thus have $\left(\frac{dA}{dT}\right)_v$ expressed in terms of a definite, instead of an indefinite integral. Substituting from (48) the value of $\left(\frac{dA}{dT}\right)_v$ in (36) we have instead of (39) and (40)

$$A = H_v - T\int_0^T \frac{1}{T}\frac{dH}{dT}dT = H_v - T\int_0^T \frac{(C_1 - C_2)}{T}dT. \tag{49}$$

The assumption of Nernst is therefore sufficient to convert the indefinite integrals of (39) and (40) into the definite integrals of (49) and therefore give us an expression in which A is determined unambiguously in terms of H_v, C_1, C_2, etc.

In the original statement and discussion of the Nernst heat theorem, Nernst assumed that the specific heats of solids could be expressed by an infinite series of ascending powers of the temperature; in fact, he assumed that only two or three terms of the series were necessary with the result that the specific heats were supposed to be given by linear or parabolic functions of the temperature. Recent work has shown that such a procedure is open

to grave objections, if the formulas deduced are applied over considerable ranges of temperature. In order to obtain accurate results, the formulas of Nernst and Lindemann or of Debye for the specific heats must be used. Since however the methods used by Nernst in his earlier applications of the heat theorem are of considerable interest and value, it may be advisable to discuss the applications of the heat theorem according to Nernst's original methods. We shall therefore assume with Nernst that the heat of a reaction H_p in a condensed system can be expressed in the following form:

$$H_p = H_0 + aT + bT^2 + cT^3 + \cdots . \tag{50}$$

Substituting this value of H in equation (38), we obtain on integration

$$A = H_0 - aT \log T - bT^2 - \frac{c}{2}T^3 + \cdots + IT, \tag{51}$$

where I is the constant of integration. From (51) we obtain for $\left(\frac{dA}{dT}\right)_p$,

$$\left(\frac{dA}{dT}\right)_p = -a - a \log T - 2\,bT - \frac{3}{2}cT^2 + \cdots + I. \tag{52}$$

According to Nernst's theorem, when

$$T = 0, \quad \left(\frac{dA}{dT}\right) = 0.$$

Hence $a = 0$ and $I = 0$ and therefore

$$\left(\frac{dA}{dT}\right)_p = -2\,bT - \frac{3}{2}cT^2 \cdots . \tag{53}$$

Similarly, since $a = 0$, and $I = 0$, from equations (50) and (51) we have

$$\left.\begin{aligned} H_p &= H_0 + bT^2 + cT^3 + \cdots \\ A &= H_0 - bT^2 - \frac{c}{2}T^3 \cdots \\ \left(\frac{dH_p}{dT}\right)_p &= 2\,bT + 3\,cT^2 + \cdots \end{aligned}\right\} \tag{54}$$

Evidently at the absolute zero

$$\left(\frac{dH_p}{dT}\right)_p = 0 = C_1 - C_2,$$

or the heat capacity of the initial substances is equal to that of the products.

If we assume that the molecular heat of a solid can be expressed in the following form:

$$C_p = \alpha_0 + 2\beta_0 T + 3\gamma_0 T^2 + \cdots, \tag{55}$$

then the value of $\left(\frac{dH_p}{dT}\right)_p$ is evidently

$$\left(\frac{dH_p}{dT}\right)_p = C_1 - C_2 = -\sum \nu\alpha_0 - 2\sum \nu\beta_0 T - 3\sum \nu\gamma_0 T^2 + \cdots$$
$$= 2bT + 3cT^2 + \cdots, \tag{56}$$

where, in the summation, the molecular heats of the products are taken as positive and those of the initial substances as negative. From (56) we get the following relations:

$$\left.\begin{aligned} \sum \nu\alpha_0 &= 0 \\ \sum \nu\beta_0 &= -b \\ \sum \nu\gamma_0 &= -c. \end{aligned}\right\} \tag{57}$$

Thus the expressions for H_p and A may be written

$$\left.\begin{aligned} H_p &= H_0 - \sum \nu\beta_0 T^2 - \sum \nu\gamma_0 T^3 \cdots \\ A &= H_0 + \sum \nu\beta_0 T^2 + \sum \nu\gamma_0 \frac{T^3}{2} + \cdots \end{aligned}\right\} \tag{58}$$

Transformation of Monoclinic into Rhombic Sulphur

From the values of the specific heats of monoclinic and rhombic sulphur, Nernst finds, using equations (54) and (56) in the abbreviated forms, $H_p = H_0 + bT^2$ and

$$\frac{dH_p}{dT} = 2bT,$$

that $b = 1.15 \times 10^{-5}$. From the known value of H_p at ordinary temperatures for the transformation of 1 gram of monoclinic into rhombic sulphur, he obtains

$$H_p = 1.57 + 1.15 \times 10^{-5} T^2. \tag{59}$$

The following table illustrates the applicability of equation (59).

T	H_p calc.	H_p observed	Observer
273	2.40	2.43	Brönsted
368	3.19	3.13	Tammann

Applying also the second equation in (54), we have

$$A = 1.57 - 1.15 \times 10^{-5} T^2. \tag{60}$$

Now at the transition temperature of the two modifications, $A = 0$. Putting this value in equation (60) we obtain for the transition temperature the value

$$T_0 = \sqrt{\frac{1.57}{1.15 \times 10^{-5}}} = 369.5^\circ \text{ absolute},$$

whereas the observed transition temperature is 95.4° C. = 368.4° absolute.

Similarly the melting point of a substance can be calculated from a knowledge of the latent heat of fusion and of the specific heats as functions of the temperature.

Application to Homogeneous Gaseous Reactions

We shall omit further consideration of condensed systems and proceed to a study of the methods employed by Nernst to extend his theorem to equilibria in gaseous systems. We shall first consider a reaction among gases, each one of which is in equilibrium with its solid form. Since the thermodynamic potential of a solid is equal to that of an equal mass of the vapor in equilibrium with it, the affinity of a reaction among the gases is equal to the affinity of a similar reaction among the solids, for $A = \Phi_1 - \Phi_2$. The heat of the reaction, H'_p, in the gaseous phase will in

general differ from that in the condensed system, H_p. Whenever necessary, we shall distinguish quantities referring to the gaseous phase by accents. Thus we shall have

$$H'_p = H'_0 + a'T + b'T^2 + \cdots, \tag{61}$$

$$C'_p = \alpha' + 2\beta'T + 3\gamma' T^2 + \cdots. \tag{62}$$

Since $$\frac{dH'_p}{dT} = C_1 - C_2 = -\sum \nu C'_p,$$

evidently

$$H'_p = H'_0 - \sum \nu\alpha' T - \sum \nu\beta' T^2 - \sum \nu\gamma' T^3 - \cdots. \tag{63}$$

If L is the heat of sublimation of one mole of a given solid, that is, the heat evolved when one mole of the vapor condenses into a solid at constant temperature and pressure,

$$\frac{dL}{dT} = C_1 - C_2 = \text{molecular heat of vapor} - \text{molecular heat of solid}$$
$$= (\alpha' - \alpha_0) + 2(\beta' - \beta_0) T + 3(\gamma' - \gamma_0) T^2 + \cdots. \tag{64}$$

Hence by integration

$$L = L_0 + (\alpha' - \alpha_0) T + (\beta' - \beta_0) T^2 + (\gamma' - \gamma_0) T^3 + \cdots. \tag{65}$$

It is easy to show that the following relation exists between H'_p, H_p and the heats of sublimation of the various solids concerned, viz.:

$$H'_p = H_p - \sum \nu L, \tag{66}$$

where again ν is taken as positive for substances that are formed, and negative for substances which disappear in the reaction. According to equation (40) of Chap. XV,

$$\frac{d \log K_p}{dT} = -\frac{H'_p}{RT^2},$$

$$\log K_p = \int -\frac{H'_p}{RT^2} dT. \tag{67}$$

Substituting in (67) the value of H'_p as given by equation (63) and integrating, we obtain

$$RT \log K_p = H'_0 + \sum \nu\alpha' T \log T + \sum \nu\beta' T^2$$
$$+ \tfrac{1}{2} \sum \nu\gamma' T^3 + \cdots + RTI, \tag{68}$$

where I is an integration constant. According to the modified Clausius-Clapeyron formula (equation (31), Chap. X),

$$\frac{d \log p}{dT} = \frac{L}{RT^2}, \tag{69}$$

if p is the pressure of saturated vapor and L is the molar heat of sublimation. Substituting in (69) the value of L from (65) and integrating we obtain

$$RT \log p = -L_0 + (\alpha' - \alpha_0) T \log T + (\beta' -)\beta_0 T^2 + \cdots + RTi, \tag{70}$$

where i is an integration constant characteristic of the vapor pressure curve for a definite substance. Now according to equation (38) of Chap. XV, we have

$$A = RT \log K_p - RT \sum \nu \log p. \tag{71}$$

If we substitute in (71), the values of $RT \log K_p$ from equation (68) and of $RT \log p$ from equation (70) we obtain

$$A = (H'_0 + \sum \nu L_0) + \sum \nu \alpha_0 T \log T + \sum \nu \beta_0 T^2 + \frac{\sum \nu \gamma_0}{2} T^3 + \cdots + RT (I - \sum \nu i). \tag{72}$$

Now the affinity of the gaseous reaction is as we have said equal to that of the reaction in the condensed system and the latter is given by equation (58), that is

$$A = H_0 + \sum \nu \beta_0 T^2 + \frac{\sum \nu \gamma_0}{2} T^3 + \cdots. \tag{58}$$

Comparing (58) and (72) we have

$$\left.\begin{aligned} H'_0 + \sum \nu L_0 &= H_0, \\ \sum \nu \alpha_0 &= 0, \\ I &= \sum \nu i. \end{aligned}\right\} \tag{73}$$

Of the three relations in (73), the first is in agreement with equation (66) and the second is in harmony with the first relation

in (57). The third relation is new and states that the integration constant of equation (68) can be calculated from the integration constants represented by i in equation (70). A thorough knowledge of the vapor pressure curve of any solid concerned in the reaction will give the value of the integration constant i. Hence the problem of calculating the affinity or the equilibrium constant in a gaseous reaction (and to do this requires a knowledge of the integration constant I of equation (68)) can be solved if, on the basis of experiment, we can determine the integration constant i of equation (70) for the solid form of each gaseous substance. Substituting the relation $I = \sum \nu i$ from equations (73) in (68) we obtain for the equilibrium constant of a reaction in a gaseous system,

$$\log_{10} K_p = \frac{H'_0}{4.574\,T} + \frac{\sum \nu\alpha' \log_{10} T}{1.987} + \frac{\sum \nu\beta' T}{4.574} + \frac{\sum \nu\gamma' T^2}{9.15} + \cdots + \frac{\sum \nu i}{2.303}. \tag{74}$$

The quantity $\frac{i}{2.303} = C_0$ is called by Nernst the chemical constant of any particular substance. Nernst assumes that the value of α' may be put equal to 3.5. This gives us the following somewhat simplified equations, instead of (62), (63) and (74):

$$C'_p = 3.5 + 2\,\beta' T + 3\,\gamma' T^2. \tag{75}$$

$$H'_p = H'_0 - \sum \nu\, 3.5\, T - \sum \nu\beta' T^2 - \sum \nu\gamma' T^3. \tag{76}$$

$$\log_{10} K_p = \frac{H'_0}{4.574\,T} + \sum \nu\, 1.75 \log_{10} T + \frac{\sum \nu\beta' T}{4.574} + \frac{\sum \nu\gamma' T^2}{9.15} + \sum \nu C_0. \tag{77}$$

For a discussion of the methods employed by Nernst in calculating the chemical constants, reference must be made to his Thermodynamics and Chemistry, Chap. VII. It must suffice to give here a table of the chemical constants according to Nernst.

TABLE XXXIV

Chemical constants

H_2	2.2	N_2O	3.3	CCl_4	3.1
CH_4	2.5	H_2S	3.0	$CHCl_3$	3.2
N_2	2.6	SO_2	3.3	C_6H_6	3.1
O_2	2.8	CO_2	3.2	C_2H_5OH	4.1
CO	3.6	CS_2	3.1	Ether	3.3
Cl_2	3.0	NH_3	3.3	Acetone	3.7
HCl	3.0	H_2O	3.7	Propyl acetate	3.8
NO	3.7				

Dissociation of Water Vapor

We shall apply the above formulas to the reaction $2\,H_2O \rightleftarrows 2H_2 + O_2$ for which Nernst gives the following data:

$$\left.\begin{array}{l} C'_p \text{ for } H_2O = 8.02 \\ C'_p \text{ for } H_2 \text{ and } O_2 = 6.9 \end{array}\right\} \text{ at } T = 450.$$

$$\sum \nu = 1;\ \sum \nu C_0 \text{ (from Table XXXIV)} = 4.4 + 2.8 - 7.4 = -0.2.$$

$$\frac{dH'_p}{dT} = 16.04 - 20.7 = -4.66 = -3.5 - 2\,\beta' T \ (T = 450).$$

Hence $\beta' = 0.0013$. Nernst gives $H'_p = -116{,}000$ at $T = 373$. Accordingly $-116{,}000 = H'_0 - 3.5\,T - 0.0013\,T^2$ $(T = 373)$. This gives $H'_0 = -114{,}500$. We accordingly have on substituting these values in (77),

$$\log_{10} K_p = -\frac{25{,}030}{T} + 1.75 \log T + 0.00028\,T - 0.2. \quad (78)$$

If x denotes the very small degree of dissociation of the water vapor at atmospheric pressure,

$$K_p = \frac{x^3}{2\,(1-x)^2\left(1+\frac{x}{2}\right)} = \frac{x^3}{2} \text{ (very approximately).} \quad (79)$$

Since $3 \log_{10} x = \log_{10} K_p + \log_{10} 2 = \log_{10} K_p + 0.301$, we may write in place of (78),

$$3 \log_{10} x = -\frac{25{,}030}{T} + 1.75 \log_{10} T + 0.00028\,T + 0.1. \quad (80)$$

In the following table are given the observed temperatures corresponding to given values of x as determined by Nernst and Wartenberg and the values of T as calculated from equation (80). The agreement is considered by Nernst to be good.

$100\,x$	T (observed)	T (calculated)
0.0189	1480	1455
0.199	1800	1745

From equation (80) we calculate the degree of dissociation of water vapor at 17° C. (assumed to be under atmospheric pressure) to be $x = 10^{-27.27}$ or $100\,x = 10^{-25.27}$. If p is the pressure of saturated vapor at 17° C., $x = \frac{10^{-27.27}}{p^{\frac{1}{3}}}$ where p is expressed in atmospheres.

Application of the Nernst and Lindemann Formula

We shall now proceed to calculate the value of A employing the Nernst and Lindemann expression for the specific heat of a solid and also their empirical expression $C_p = C_v + aT^{\frac{3}{2}}$ for the relation between C_p and C_v. If n represents the number of moles of a given solid substance taking part in a reaction and if n is positive if the substance is formed and negative if it disappears in the reaction, we evidently have

$$\frac{dH_p}{dT} = (C_1 - C_2) = -\sum nC_p = -\sum nC_v - \sum naT^{\frac{3}{2}}.$$

Substituting in equation (49) we obtain

$$A = H_p + T\int_0^T \frac{\sum nC_v}{T}\,dT + T\int_0^T \frac{\sum naT^{\frac{3}{2}}}{T}\,dT. \qquad (81)$$

If we insert in (81) the value of C_v as given by equation (28) we obtain on integration

$$A = H_p + \frac{3}{2}\sum nRT\left[\frac{\frac{\beta\nu}{T}}{e^{\frac{\beta\nu}{T}} - 1} + \frac{\frac{\beta\nu}{2T}}{e^{\frac{\beta\nu}{2T}} - 1} - \log\left(1 - e^{-\frac{\beta\nu}{T}}\right)\left(1 - e^{-\frac{\beta\nu}{2T}}\right)\right] + \frac{2}{3}\sum naT^{\frac{3}{2}}. \qquad (82)$$

If H_0 is the value of H_ν at the absolute zero, we must have, since

$$\frac{dH_\nu}{dT} = (C_1 - C_2)_\nu = -\sum nC_\nu,$$

$$H_\nu = H_0 - \sum n \int_0^T C_\nu dT = H_0 - \sum n \int_0^T C_v dT - \sum n \int_0^T aT^{\frac{3}{2}}\, dT. \tag{83}$$

Employing again equation (28) we obtain

$$H_\nu = H_0 - \frac{3}{2}\sum nRT \left[\frac{\frac{\beta\nu}{T}}{e^{\frac{\beta\nu}{T}} - 1} + \frac{\frac{\beta\nu}{2T}}{e^{\frac{\beta\nu}{2T}} - 1} \right] - \frac{2}{5}\sum naT^{\frac{3}{2}}. \tag{84}$$

Substituting this value of H_ν in equation (82) we have

$$A = H_0 - \frac{3}{2}\sum nRT \left[\log \left(1 - e^{-\frac{\beta\nu}{T}}\right)\left(1 - e^{-\frac{\beta\nu}{2T}}\right) \right] + \frac{4}{15}\sum naT^{\frac{3}{2}}. \tag{85}$$

The equations just developed are ordinarily applied in the following manner. The characteristic frequencies of all the solid substances are obtained by calculation or otherwise. From the experimental value of H_ν at any temperature, H_0 is calculated using equation (84). Then by means of (82) or (85) the value of A, the affinity of the process is obtained. The value of a in the equation $C_\nu = C_v + aT^{\frac{3}{2}}$ must be known or estimated for each substance. The task of applying equations (82), (84) and (85) is much facilitated if one employs the tables to be found at the end of this chapter.

We have already dwelt on the fact that at the present time the investigations of Debye are regarded as having given expressions for the energy and specific heat of solids which have a sound theoretical basis and which also represent the facts with considerable fidelity. We shall therefore develop very briefly these expressions in a form suitable for use in testing Nernst's Heat Theorem.

Combining equations (32a) and (24), we have

$$U = U_0 + \frac{3}{4}R\beta\nu \left[\frac{4\pi^4}{5x^4} - 12 \sum_{n=1}^{n=\infty} e^{-nx} \left(\frac{1}{nx} + \frac{3}{n^2x^2} + \frac{6}{n^3x^3} + \frac{6}{n^4x^4} \right) \right]. \tag{86}$$

From the equation

$$F = U - TS = U + T\left(\frac{dF}{dT}\right)_v,$$

where F is the free energy, we easily obtain

$$F = -T\int^T \frac{U}{T^2}\,dT.$$

Substituting the value of U from equation (32a) and changing from T to x as the variable, we obtain on integration the two following equivalent expressions:

$$F = U_0 - 9\,RT\left[\frac{2.1646}{x^3} - \sum e^{-nx}\left(\frac{1}{n^2x} + \frac{2}{n^3x^2} + \frac{2}{n^4x^3}\right)\right]. \quad (87a)$$

$$F = U_0 - 9\,RT\left[\frac{C_v}{36\,C_\infty} + \frac{x}{12\,(e^x - 1)} - \frac{1}{3}\log_e(1 - e^{-x})\right]. \quad (87b)$$

At very low temperatures (x being large) we see from (32a) and (87b) that we may write

$$U = U_0 + \frac{C_vT}{4}; \qquad F = F_0 - \frac{C_vT}{12}.$$

If we neglect the changes in volume which occur during the reaction and if therefore we neglect the difference between C_p and C_v, the heat, H_p, evolved in the reaction will be given by $-\sum nU$ and the affinity A by $-\sum nF$ where n is the number of moles of a given substance, positive if it refers to a product of the reaction. We accordingly obtain from (32a) and (87b),

$$H_p = H_0 - \sum n \cdot \frac{3\,RT}{4}\left(\frac{C_v}{C_\infty} + \frac{3\,x}{e^x - 1}\right).$$

$$A = H_0 + \sum n \cdot \frac{RT}{4}\left[\frac{C_v}{C_\infty} + \frac{3\,x}{e^x - 1} - 12\log_e(1 - e^{-x})\right].$$

If we now introduce the correction terms which take account of the difference between C_p and C_v, we shall have, as in equations (82), (83), (84) and (85),

$$H_p = H_0 - \sum n\,\frac{3\,RT}{4}\left(\frac{C_v}{C_\infty} + \frac{3\,x}{e^x - 1}\right) - \frac{2}{5}\sum naT^{\frac{5}{2}}. \quad (88)$$

$$A = H_0 + \sum n \frac{RT}{4}\left(\frac{C_v}{C_\infty} + \frac{3x}{e^x - 1} - 12 \log_e (1 - e^{-x})\right) + \frac{4}{15}\sum naT^{\frac{3}{2}}. \quad (89)$$

$$A = H_p + \sum nRT\left(\frac{C_v}{C_\infty} + \frac{3x}{e^x - 1} - 3 \log_e (1 - e^{-x})\right) + \frac{2}{3}\sum naT^{\frac{3}{2}}. \quad (90)$$

At very low temperatures, $C_v = kT^3$ (see equation (35)). For reactions at low temperatures, equations (88) and (89) become (since $C_\infty = 3R$ and x is very large).

$$H_p = H_0 - \sum n \frac{C_v T}{4} = H_0 - \sum \frac{nkT^4}{4}. \quad (88a)$$

$$A = H_0 + \sum n \frac{C_v T}{12} = H_0 + \sum \frac{nkT^4}{12}. \quad (89a)$$

If we represent the function $\frac{3RT}{4}\left(\frac{C_v}{C_\infty} + \frac{3x}{e^x - 1}\right)$ by E, and the function $\frac{RT}{4}\left(\frac{C_v}{C_\infty} + \frac{3x}{e^x - 1} - 12 \log (1 - e^{-x})\right)$ by F, we may write equations (88), (89) and (90) as follows:

$$H_p = H_0 - \sum nE - \frac{2}{5}\sum naT^{\frac{3}{2}}. \quad (88b)$$

$$A = H_0 + \sum nF + \frac{4}{15}\sum naT^{\frac{3}{2}}. \quad (89b)$$

$$A = H_p + \sum n(E + F) + \frac{2}{3}\sum naT^{\frac{3}{2}}. \quad (90a)$$

The functions $\frac{E}{T}$ and $\frac{F}{T}$ will be found tabulated for various values of x in Tables XLII and XLIII at the end of this chapter, so that the calculations in any given case are very simple. For purposes of illustration let us consider the reaction $Ag + I \rightarrow AgI$ at the temperature T. The values of ν for each of the substances must be known and also the values of a in the expressions $C_p = C_v + aT^{\frac{3}{2}}$. From the tables we find, corresponding to the

values of $\frac{\beta\nu}{T}$, the values of $\frac{E}{T}$ and $\frac{F}{T}$ for each of the substances. (Note that $\frac{E}{T}$ and $\frac{F}{T}$ for one mole of AgI will be twice that obtained from the tables which give results for a gram-atom.) We multiply the values of $\frac{E}{T}$ and $\frac{F}{T}$ by T and obtain the functions E and F. Substituting in equations (88), (89) and (90), or (88b), (89b) and (90a), we obtain

$$H_p = H_0 + E_{Ag} + E_I - E_{AgI} + \tfrac{2}{5} T^{\frac{5}{2}} [a_{Ag} + a_I - a_{AgI}]. \quad (91)$$

$$A = H_0 - F_{Ag} - F_I + F_{AgI} - \tfrac{4}{15} T^{\frac{5}{2}} [a_{Ag} + a_I - a_{AgI}]. \quad (92)$$

$$A = H_p - (E + F)_{Ag} - (E + F)_I + (E + F)_{AgI} - \tfrac{2}{3} T^{\frac{5}{2}} [a_{Ag} + a_I - a_{AgI}]. \quad (93)$$

Thus from equation (91) we obtain the value of H_0 in terms of H_p, the three values of E and the correction terms (usually small). If we substitute this value of H_0 in equation (92), we obtain the value of A, the affinity of the process. As a matter of fact these equations are being frequently used to correct the values of H_p obtained by direct thermochemical methods, for in many cases the value of A can be determined (e.g., by electromotive force measurements) with great accuracy. In a number of cases Nernst and others have been able to show that the values of H_p as given by Thomsen are subject to a considerable error.

Some General Considerations

Since $A = (\Phi_1 - \Phi_2)_T$, it is easy to show that

$$\left(\frac{dA}{dT}\right)_p = (S_2 - S_1)_p \quad (94)$$

For reactions in condensed systems, Nernst's theorem leads to the conclusion that $S_2 - S_1 = 0$ at the absolute zero, or in other words that when a process takes place at the absolute zero, the entropy of the initial substances is equal to that of the final substances. Planck* has expressed the essence of Nernst's heat

* Thermodynamik, 4th Edition (1913), p. 268.

theorem by saying that, at the absolute zero, the entropy of a homogeneous solid or liquid substance is zero. Under these circumstances $S_2 - S_1$ would equal zero since both S_2 and S_1 would be zero. This more special formulation of the heat theorem has a great deal of probability in its favor, and we shall deduce therefrom certain consequences. It should however be borne in mind that if this more special statement of the theorem should prove to be invalid, the Nernst heat theorem might still be true.

Following Planck then we shall assume that, at the absolute zero, the entropy of a solid or liquid is zero. According to equation (23) of Chap. VIII for one mole of a substance

$$\left(\frac{dS}{dT}\right)_p = \frac{C_p}{T}. \tag{95}$$

If S_0 is the entropy at the absolute zero and S is the entropy at the temperature T, we obtain from equation (95) on integration at constant pressure,

$$S - S_0 = \int_0^T \frac{C_p}{T} dT. \tag{96}$$

But according to Planck's statement of the Nernst heat theorem, $S_0 = 0$ and therefore

$$S = \int_0^T \frac{C_p}{T} dT. \tag{97}$$

According to equations (26) and (28) of Chap. VIII, we have

$$\left(\frac{dS}{dp}\right)_T = -\left(\frac{dV}{dT}\right)_p, \tag{98}$$

$$\left(\frac{dC_p}{dp}\right)_T = -T\left(\frac{d^2V}{dT^2}\right)_p. \tag{99}$$

From (97), (98) and (99), we have

$$\left(\frac{dS}{dp}\right)_T = \int_0^T \frac{1}{T}\left(\frac{dC_p}{dp}\right)_T dT = -\int_0^T \left(\frac{d^2V}{dT^2}\right)_p dT = -\left(\frac{dV}{dT}\right)_p. \tag{100}$$

From (100) we obtain on integration,

$$\left(\frac{dV}{dT}\right)_p = \left(\frac{dV}{dT}\right)_p - \left(\frac{dV}{dT}\right)_p^0, \tag{101}$$

where $\left(\frac{dV}{dT}\right)_p^0$ is the value of $\left(\frac{dV}{dT}\right)_p$ at the absolute zero.

Evidently from (101) we have

$$\left(\frac{dV}{dT}\right)_p^0 = 0, \tag{102}$$

or the coefficient of expansion of a solid body becomes vanishingly small as the temperature approaches the absolute zero. This conclusion is in harmony with recent work on this subject.

Transition Points

If we consider the transition point between a liquid and a solid or between allotropic forms of a solid and write the reaction so that heat is evolved when the process proceeds as written from left to right, we shall have

$$\text{Liquid} \rightleftarrows \text{Solid} + H_p.$$

Let T_m be the transition temperature. At this temperature $A = 0$ and H_p is positive. If we assume that the course of the A and H_p curves from $T = 0$ to T_m is given approximately by equations (88a) and (89a) then evidently at the temperature T_m, $\frac{\sum n kT^4}{12}$ is negative. Now $\frac{dA}{dT} = \frac{1}{3}\sum n kT^3$ and $\frac{d^2A}{dT^2} = \sum n kT^2$. Also $\frac{dH_p}{dT} = -\sum n kT^3$, so that near the transition temperature T_m, $\frac{dA}{dT}$ and $\frac{d^2A}{dT^2}$ are negative and $\frac{dH_p}{dT}$ is positive. But $\frac{dH_p}{dT} = C_1 - C_2$, and therefore $C_1 > C_2$. At and below the transition temperature the specific heat of a liquid is greater than that of the solid. Or in general, near the transition temperature the modification which is formed with evolution of heat has the smaller heat capacity. Thus monoclinic sulphur has a greater

specific heat than rhombic sulphur below 96° C. Additional illustrations will be found in the following tables.

TABLE XXXV. SOLIDS AND LIQUIDS

Substance	C_{liq}	C_{solid}
Benzene	0.43	0.35
Lead	0.036	0.034
Bromine	0.11	0.084
Potassium	0.25	0.17
Mercury	0.034	0.032
Water	1.0	0.5

TABLE XXXVI. ALLOTROPIC FORMS OF ELEMENTS

		C			C
Graphite	−50°	0.114	Diamond	−50°	0.0635
Graphite	1000°	0.467	Diamond	1000°	0.459
Phosphorus, yellow	....	0.17–0.20	Phosphorus, red	....	0.17
Sulphur (monoclinic)	....	0.18	Sulphur (rhombic)	....	0.16

TABLE XXXVII. ALLOTROPIC MODIFICATIONS OF COMPOUNDS

Modification II is formed with evolution of heat.

	C_{I}	C_{II}
Silver iodide	0.0577	0.0544
Potassium nitrate	0.285	0.203
Ammonium nitrate	0.426	0.355

Einstein and Debye Functions

The tables at the end of this chapter will facilitate calculations depending on the use of the various functions introduced by Einstein, by Nernst and Lindemann and by Debye. In these tables, the value of $\frac{\beta\nu}{T}$ is represented by x. These tables are taken from Nernst's "Die Theoretischen und Experimen-

tellen Grundlagen des neuen Wärmesatzes," recalculated, however, for a value of $R = 1.987$ instead of $R = 1.985$ as adopted by Nernst.

Table XXXVIII contains the values of C_v for a gram-atom of a solid calculated according to equation (27):

$$C_v \text{ (Einstein)} = 3R \frac{\left(\frac{\beta\nu}{T}\right)^2 e^{\frac{\beta\nu}{T}}}{\left(e^{\frac{\beta\nu}{T}} - 1\right)^2} = 3R \cdot \frac{x^2 e^x}{(e^x - 1)^2}.$$

Table XXXIX gives the values of C_v calculated according to the formula of Debye (equation (34)).

Table XL contains the values of the Einstein function defined by the equation $\frac{E}{T} = \frac{3Rx}{e^x - 1}$ (see equation (84)).

Table XLI is devoted to the Einstein function,

$$\frac{F}{T} = -3R \log_e (1 - e^{-x}) \text{ (see equation (85)).}$$

Table XLII contains the values of the Debye function,

$$\frac{E}{T} = \frac{3R}{4}\left(\frac{C_v}{C_\infty} + \frac{3x}{e^x - 1}\right) \text{ (see equations (88) and (88b)).}$$

Table XLIII gives the values of the Debye function,

$$\frac{F}{T} = \frac{E}{3T} - 3R \log_e (1 - e^{-x}) = \frac{R}{4}\left[\frac{C_v}{C_\infty} + \frac{3x}{e^x - 1} - 12 \log_e (1 - e^{-x}\right]$$

(see equations (89) and (89b)).

TABLE XXXVIII. C_v (Einstein)

x	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0	5.961	5.953	5.941	5.917	5.882	5.838	5.785	5.723	5.653	5.574
1	5.488	5.395	5.294	5.188	5.076	4.959	4.837	4.711	4.582	4.450
2	4.316	4.180	4.043	3.906	3.768	3.630	3.493	3.356	3.222	3.089
3	2.958	2.830	2.704	2.581	2.460	2.344	2.231	2.121	2.015	1.912
4	1.813	1.717	1.625	1.538	1.452	1.371	1.293	1.219	1.149	1.082
5	1.018	0.957	0.899	0.844	0.792	0.744	0.697	0.653	0.611	0.572
6	0.536	0.500	0.466	0.436	0.407	0.379	0.354	0.330	0.307	0.286
7	0.266	0.248	0.231	0.215	0.200	0.185	0.172	0.160	0.149	0.138
8	0.128	0.119	0.110	0.102	0.0945	0.0884	0.0811	0.0752	0.0695	0.0650
9	0.0600	0.0554	0.0509	0.0468	0.0435	0.0400	0.0372	0.0340	0.0310	0.0286
10	0.0266	0.0247	0.0231	0.0212	0.0196	0.0180	0.0167	0.0152	0.0142	0.0129
11	0.0119	0.0110	0.0102	0.0093	0.0085	0.0078	0.0073	0.0067	0.0062	0.0057
12	0.0052	0.0048	0.0045	0.0041	0.0038	0.0035	0.0032	0.0029	0.0027	0.0024
13	0.0022	0.0020	0.0019	0.0017	0.0016	0.0015	0.0014	0.0013	0.0012	0.0011

TABLE XXXIX. C_v (Debye)

x	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0	5.961	5.96	5.95	5.94	5.92	5.89	5.86	5.82	5.78	5.74
1	5.676	5.62	5.55	5.49	5.42	5.35	5.27	5.19	5.10	5.01
2	4.919	4.83	4.74	4.65	4.55	4.44	4.34	4.24	4.14	4.04
3	3.945	3.84	3.74	3.65	3.55	3.45	3.36	3.27	3.18	3.09
4	2.999	2.91	2.83	2.75	2.67	2.59	2.51	2.43	2.35	2.27
5	2.200	2.13	2.06	2.00	1.94	1.88	1.82	1.76	1.70	1.64
6	1.583	1.53	1.48	1.43	1.38	1.34	1.30	1.26	1.22	1.18
7	1.138	1.103	1.068	1.034	1.001	0.969	0.938	0.908	0.880	0.854
8	0.831	0.811	0.791	0.771	0.751	0.732	0.713	0.694	0.675	0.656
9	0.637	0.618	0.599	0.580	0.561	0.542	0.524	0.506	0.487	0.469
10	0.451	0.435	0.421	0.409	0.398	0.388	0.378	0.368	0.359	0.351
11	0.343	0.335	0.327	0.319	0.311	0.303	0.295	0.287	0.280	0.273
12	0.267	0.261	0.255	0.249	0.243	0.237	0.231	0.225	0.220	0.215
13	0.210	0.205	0.200	0.196	0.192	0.188	0.184	0.180	0.176	0.172
14	0.168	0.164	0.161	0.158	0.155	0.152	0.149	0.146	0.143	0.140
15	0.137	0.134	0.131	0.128	0.125	0.123	0.121	0.119	0.117	0.115

x		x		x	
16	0.113	21	0.0499	26	0.0262
17	0.094	22	0.0433	27	0.0234
18	0.079	23	0.0380	28	0.0211
19	0.067	24	0.0335	29	0.0189
20	0.058	25	0.0296	30	0.0172

TABLE XLa. $\frac{E}{T}$ (Einstein). x from 0 to 2.00

x	0	1	2	3	4	5	6	7	8	9
0.0	5.961	5.931	5.902	5.873	5.844	5.815	5.786	5.756	5.727	5.798
0.1	5.669	5.640	5.611	5.582	5.554	5.526	5.498	5.470	5.441	5.413
0.2	5.385	5.357	5.329	5.301	5.273	5.245	5.218	5.191	5.164	5.137
0.3	5.111	5.085	5.058	5.032	5.006	4.979	4.953	4.926	4.900	4.874
0.4	4.848	4.822	4.796	4.770	4.745	4.720	4.695	4.670	4.644	4.619
0.5	4.594	4.569	4.544	4.519	4.494	4.469	4.445	4.421	4.397	4.373
0.6	4.349	4.325	4.301	4.277	4.254	4.231	4.207	4.184	4.161	4.138
0.7	4.115	4.092	4.069	4.047	4.024	4.002	3.979	3.957	3.935	3.913
0.8	3.891	3.869	3.847	3.825	3.803	3.781	3.759	3.738	3.717	3.696
0.9	3.675	3.654	3.634	3.613	3.593	3.573	3.552	3.531	3.511	3.490
1.0	3.469	3.448	3.428	3.408	3.388	3.368	3.348	3.328	3.309	3.290
1.1	3.271	3.252	3.233	3.213	3.194	3.175	3.156	3.137	3.319	3.101
1.2	3.083	3.065	3.047	3.029	3.011	2.993	2.975	2.957	2.939	2.921
1.3	2.903	2.885	2.868	2.851	2.834	2.817	2.800	2.783	2.766	2.749
1.4	2.732	2.715	2.698	2.681	2.664	2.648	2.632	2.616	2.600	2.584
1.5	2.568	2.553	2.537	2.521	2.505	2.489	2.473	2.457	2.442	2.427
1.6	2.412	2.397	2.382	2.367	2.352	2.337	2.322	2.307	2.293	2.279
1.7	2.265	2.251	2.236	2.222	2.208	2.194	2.180	2.166	2.152	2.138
1.8	2.124	2.110	2.096	2.083	2.070	2.057	2.044	2.031	2.018	2.005
1.9	1.992	1.979	1.966	1.953	1.940	1.928	1.916	1.903	1.891	1.878

TABLE XLb. $\frac{E}{T}$ (Einstein). x from 0 to 12.0

x	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0	5.961	5.669	5.385	5.111	4.848	4.594	4.349	4.115	3.891	3.675
1	3.469	3.271	3.083	2.903	2.732	2.568	2.412	2.265	2.124	1.992
2	1.866	1.747	1.635	1.529	1.428	1.333	1.243	1.159	1.081	1.007
3	0.937	0.872	0.811	0.754	0.700	0.650	0.603	0.560	0.519	0.480
4	0.444	0.411	0.381	0.352	0.326	0.301	0.278	0.257	0.237	0.219
5	0.202	0.186	0.172	0.158	0.146	0.134	0.124	0.114	0.106	0.098
6	0.0891	0.0818	0.0752	0.0691	0.0635	0.0584	0.0536	0.0492	0.0452	0.0415
7	0.0380	0.0349	0.0320	0.0294	0.0269	0.0248	0.0227	0.0208	0.0190	0.0174
8	0.0160	0.0146	0.0134	0.0123	0.0113	0.0103	0.0094	0.0086	0.0079	0.0072
9	0.0066	0.0061	0.0055	0.0050	0.0046	0.0042	0.0039	0.0035	0.0032	0.0030
10	0.0027	0.0025	0.0023	0.0021	0.0019	0.0017	0.0016	0.0014	0.0013	0.0012
11	0.0011	0.0010	0.0009	0.0008	0.0008	0.0007	0.0006	0.0006	0.0005	0.0005
12	0.0004	....	....	....	....	....	....	....	....	....

TABLE XLIa. $\frac{F}{T}$ (Einstein). x from 0 to 2.00

x	0	1	2	3	4	5	6	7	8	9
0.1	14.02	13.45	12.94	12.48	12.08	11.69	11.33	11.00	10.69	10.43
0.2	10.18	9.93	9.69	9.45	9.22	8.99	8.78	8.58	8.39	8.22
0.3	8.05	7.88	7.72	7.56	7.41	7.27	7.14	7.00	6.87	6.74
0.4	6.62	6.51	6.40	6.29	6.18	6.07	5.96	5.86	5.76	5.66
0.5	5.56	5.47	5.38	5.28	5.19	5.10	5.02	4.95	4.88	4.81
0.6	4.74	4.66	4.59	4.52	4.45	4.39	4.32	4.26	4.20	4.14
0.7	4.08	4.02	3.97	3.92	3.86	3.81	3.76	3.71	3.66	3.61
0.8	3.55	3.51	3.47	3.42	3.38	3.34	3.29	3.25	3.21	3.16
0.9	3.11	3.07	3.03	3.00	2.96	2.93	2.88	2.85	2.81	2.77
1.0	2.734	2.695	2.658	2.623	2.590	2.559	2.528	2.498	2.468	2.440
1.1	2.411	2.382	2.354	2.326	2.299	2.272	2.245	2.217	2.190	2.163
1.2	2.136	2.109	2.083	2.058	2.034	2.010	1.986	1.963	1.940	1.918
1.3	1.896	1.874	1.852	1.830	1.809	1.788	1.768	1.748	1.728	1.708
1.4	1.688	1.669	1.650	1.631	1.612	1.593	1.574	1.556	1.538	1.521
1.5	1.504	1.487	1.471	1.455	1.439	1.423	1.407	1.391	1.375	1.359
1.6	1.343	1.328	1.313	1.298	1.284	1.270	1.256	1.242	1.228	1.215
1.7	1.201	1.188	1.174	1.161	1.149	1.136	1.124	1.112	1.100	1.088
1.8	1.076	1.064	1.052	1.041	1.030	1.018	1.006	0.995	0.984	0.973
1.9	0.963	0.953	0.942	0.931	0.921	0.911	0.901	0.892	0.883	0.874

TABLE XLIb. $\frac{F}{T}$ (Einstein). x from 0 to 7.0

x	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0	∞	14.020	10.180	8.049	6.615	5.565	4.745	4.085	3.550	3.109
1	2.734	2.411	2.136	1.896	1.688	1.504	1.343	1.201	1.076	0.963
2	0.865	0.777	0.699	0.629	0.566	0.510	0.458	0.412	0.372	0.335
3	0.302	0.273	0.246	0.222	0.200	0.181	0.164	0.148	0.133	0.119
4	0.107	0.097	0.088	0.079	0.071	0.064	0.058	0.052	0.047	0.042
5	0.038	0.034	0.031	0.028	0.025	0.022	0.020	0.018	0.016	0.014
6	0.013	0.011	0.009	0.008	0.007	0.006	0.005	0.004	0.004	0.003
7	0.003	....	....	....	....	....	....	....	....	....

TABLE XLIIa. $\frac{E}{T}$ (Debye). x from 0 to 2.00

x	0	1	2	3	4	5	6	7	8	9
0.1	5.739	5.716	5.694	5.673	5.652	5.631	5.610	5.589	5.568	5.547
0.2	5.526	5.506	5.485	5.464	5.443	5.422	5.401	5.380	5.359	5.338
0.3	5.317	5.296	5.276	5.255	5.235	5.215	5.195	5.175	5.155	5.135
0.4	5.115	5.096	5.076	5.056	5.036	5.017	4.997	4.977	4.957	4.937
0.5	4.917	4.897	4.878	4.859	4.840	4.821	4.792	4.783	4.764	4.745
0.6	4.726	4.708	4.689	4.670	4.651	4.632	4.614	4.596	4.578	4.559
0.7	4.540	4.522	4.504	4.487	4.469	4.451	4.433	4.416	4.398	4.380
0.8	4.362	4.345	4.328	4.311	4.294	4.277	4.259	4.242	4.225	4.207
0.9	4.190	4.173	4.156	4.139	4.122	4.105	4.088	4.071	4.054	4.037
1.0	4.021	4.005	3.989	3.972	3.956	3.939	3.922	3.906	3.890	3.874
1.1	3.858	3.842	3.826	3.810	3.794	3.778	3.762	3.746	3.730	3.714
1.2	3.699	3.684	3.669	3.654	3.639	3.624	3.609	3.594	3.579	3.564
1.3	3.549	3.534	3.519	3.504	3.490	3.475	3.460	3.445	3.431	3.417
1.4	3.402	3.388	3.374	3.360	3.346	3.332	3.318	3.304	3.290	3.276
1.5	3.262	3.248	3.234	3.220	3.206	3.193	3.179	3.166	3.153	3.139
1.6	3.126	3.113	3.099	3.085	3.072	3.059	3.046	3.033	3.020	3.007
1.7	2.995	2.982	2.969	2.956	2.943	2.930	2.918	2.905	2.893	2.880
1.8	2.867	2.854	2.842	2.829	2.817	2.804	2.792	2.779	2.767	2.755
1.9	2.742	2.730	2.719	2.707	2.695	2.684	2.673	2.662	2.651	2.640

TABLE XLIIb. $\frac{E}{T}$ (Debye). x from 0 to 16.0

x	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0	5.961	5.739	5.526	5.317	5.115	4.917	4.726	4.540	4.362	4.190
1	4.021	3.858	3.699	3.549	3.402	3.262	3.126	2.995	2.867	2.742
2	2.626	2.516	2.409	2.307	2.207	2.110	2.019	1.931	1.846	1.766
3	1.689	1.615	1.544	1.477	1.413	1.353	1.295	1.239	1.185	1.133
4	1.083	1.037	0.994	0.953	0.913	0.874	0.837	0.801	0.766	0.732
5	0.702	0.672	0.644	0.619	0.595	0.571	0.548	0.526	0.504	0.483
6	0.462	0.444	0.426	0.409	0.393	0.379	0.366	0.352	0.339	0.326
7	0.313	0.302	0.291	0.281	0.270	0.261	0.252	0.242	0.234	0.227
8	0.220	0.214	0.208	0.202	0.196	0.191	0.186	0.180	0.175	0.169
9	0.164	0.159	0.154	0.149	0.144	0.138	0.134	0.129	0.124	0.120
10	0.1150	0.1108	0.1071	0.1039	0.1010	0.0984	0.0958	0.0932	0.0908	0.0887
11	0.0867	0.0846	0.0825	0.0805	0.0784	0.0764	0.0743	0.0723	0.0705	0.0687
12	0.0672	0.0656	0.0641	0.0626	0.0611	0.0596	0.0581	0.0566	0.0553	0.0540
13	0.0527	0.0515	0.0503	0.0491	0.0481	0.0471	0.0461	0.0451	0.0441	0.0431
14	0.0420	0.0411	0.0403	0.0395	0.0388	0.0380	0.0373	0.0365	0.0358	0.0350
15	0.0343	0.0335	0.0328	0.0320	0.0313	0.0308	0.0303	0.0298	0.0293	0.0288

TABLE XLIIIa. $\frac{F}{T}$ (Debye). x from 0 to 2.00

x	0	1	2	3	4	5	6	7	8	9
0.1	15.93	15.47	15.02	14.57	14.15	13.75	13.40	13.05	12.71	12.36
0.2	12.02	11.74	11.51	11.28	11.04	10.81	10.58	10.37	10.18	9.99
0.3	9.82	9.65	9.50	9.35	9.20	9.05	8.90	8.75	8.60	8.46
0.4	8.32	8.19	8.07	7.96	7.84	7.73	7.62	7.51	7.41	7.30
0.5	7.20	7.10	7.00	6.90	6.81	6.72	6.63	6.55	6.47	6.39
0.6	6.32	6.24	6.16	6.09	6.01	5.94	5.87	5.80	5.73	5.66
0.7	5.60	5.53	5.47	5.41	5.35	5.29	5.24	5.18	5.13	5.07
0.8	5.011	4.960	4.910	4.860	4.809	4.759	4.709	4.659	4.609	4.558
0.9	4.508	4.462	4.416	4.370	4.326	4.282	4.240	4.200	4.160	4.121
1.0	4.081	4.042	4.003	3.964	3.925	3.887	3.848	3.809	3.771	3.735
1.1	3.699	3.664	3.629	3.594	3.560	3.527	3.495	3.462	3.430	3.399
1.2	3.368	3.338	3.308	3.278	3.248	3.218	3.189	3.161	3.134	3.106
1.3	3.079	3.052	3.025	2.999	2.972	2.945	2.919	2.894	2.870	2.846
1.4	2.822	2.799	2.776	2.753	2.729	2.706	2.683	2.660	2.637	2.615
1.5	2.593	2.571	2.550	2.529	2.508	2.487	2.466	2.446	2.426	2.406
1.6	2.386	2.367	2.348	2.330	2.312	2.293	2.275	2.257	2.238	2.220
1.7	2.201	2.183	2.166	2.149	2.132	2.116	2.099	2.082	2.065	2.049
1.8	2.033	2.018	2.003	1.987	1.971	1.956	1.941	1.926	1.910	1.895
1.9	1.880	1.865	1.851	1.837	1.823	1.809	1.795	1.781	1.768	1.755

TABLE XLIIIb. $\frac{F}{T}$ (Debye). x from 0 to 15.0

x	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0	∞	15.93	12.02	9.82	8.32	7.20	6.320	5.605	5.011	4.508
1	4.081	3.699	3.368	3.079	2.822	2.593	2.386	2.201	2.033	1.880
2	1.743	1.617	1.503	1.399	1.302	1.214	1.133	1.058	0.990	0.926
3	0.8673	0.8130	0.7627	0.7164	0.6738	0.6330	0.5960	0.5618	0.5293	0.4997
4	0.4713	0.4453	0.4214	0.3989	0.3778	0.3580	0.3392	0.3215	0.3047	0.2888
5	0.2742	0.2608	0.2478	0.2363	0.2253	0.2148	0.2049	0.1953	0.1862	0.1773
6	0.1689	0.1611	0.1539	0.1471	0.1409	0.1352	0.1299	0.1247	0.1197	0.1147
7	0.1098	0.1056	0.1015	0.0975	0.0938	0.0902	0.0869	0.0836	0.0805	0.0777
8	0.0752	0.0731	0.0710	0.0690	0.0670	0.0650	0.0630	0.0610	0.0591	0.0573
9	0.0555	0.0537	0.0519	0.0501	0.0483	0.0466	0.0449	0.0433	0.0417	0.0401
10	0.0386	0.0371	0.0358	0.0348	0.0338	0.0329	0.0320	0.0311	0.0303	0.0296
11	0.0289	0.0282	0.0275	0.0268	0.0261	0.0254	0.0247	0.0241	0.0235	0.0229
12	0.0224	0.0218	0.0213	0.0208	0.0203	0.0198	0.0193	0.0188	0.0184	0.0180
13	0.0175	0.0171	0.0167	0.0164	0.0160	0.0157	0.0154	0.0150	0.0147	0.0144
14	0.0140	0.0137	0.0134	0.0132	0.0129	0.0126	0.0124	0.0122	0.0119	0.0117

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